A Novel Approach to FAME Biodiesel Production by means of Reactive Distillation

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Synopsis

Diesel engines are ubiquitous in the modern economy, but associated with resource depletion and pollution concerns, including the emission of carbon dioxide from fossil reserves. With this in mind and the fact that a diesel engine can run, with slight modifications, on biodiesel, it may be argued that biodiesel production offers a potentially sustainable way of providing motive energy whilst replacing fossil fuels.

Current biodiesel production methods revolve around the transesterification reaction in which vegetable oil is mixed with methanol in the presence of a catalyst to produce biodiesel. Often this method involves using 1.5 times to double the stoichiometric amount of required methanol. The excess amount of methanol allows the forward reaction to proceed. Novel methods have recently been examined in literature, using reactive distillation in order to reduce the excess methanol. The excess methanol, besides being dangerous to humans, has environmental concerns as well as additional cost implications.

A novel concept of reactive distillation is examined in this dissertation. The design and construction of a rig to test the novel set-up were executed. The design of the rig was based on residence times selected for the rig's three main sections; the pre-reactor, the column and the reboiler. The rig was designed as a continuous process, provided feed could be supplied constantly even in the case of small scale users. The reactor was designed to perform around a flowrate of 5*l/hr*. The main aim of the design was to produce biodiesel by using a stoichiometric feed ratio.

The apparatus was also designed on a significantly larger scale than in current literature. The rig differed in that a packed column was used instead of trays. Sand packing was used to regulate liquid flow and not gas flow. A small high surface area packing was made available to test for possible increases in conversion. Although the rig differed it was of interest that it performs as well as current production set-ups found in literature.

Commissioning sets of experiments were performed in order to resolve any operational problems encountered when operating new equipment with novel features. Variables such as temperature, packing, molar ratio and residence time were considered and their effects reported. In order to cope with difficulties associated with sample analysis a method which utilised viscosity as a measure of conversion was developed and proved. Various other batch experiments were also performed to facilitate in the design scope as well as to determine what, in terms of conversion, could be expected from the rig. The solubility of methanol in the products was also considered using ideal laws so as to understand the limits of using reactive distillation.

The results obtained from the 14 five-hour long experimental runs on the constructed prototype did not meet the specified requirements as conversion was well below the desired target of 95%. The general conversion returned was in the range of 50 to 65% for stoichiometric feed ratios, and 82% conversion for a run with 50% excess methanol, rendering the current configuration of the rig non-beneficial. From the results it was evident that residence time was the largest determinant of conversion within the limits set by the ratio of methanol to vegetable oil in the feed. Certain results proved quite fruitful while others which were expected to alter conversion returned minimal improvement.

If the development and testing of the rig were to continue, three directions of work would need to be pursued: Feed flow rates need to be controlled better; the implications of vapour-liquid equilibrium in the reboiler need to be translated into equipment changes, such as increased column vapour volume and an external condenser; and the possibility of a potential reverse reaction needs to be examined further.

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1 Introduction

1.1 Background to the research project

Current society has a great dependency on diesel fuel. If one considers general logistics, shipping, civilian transport, construction, generators and essentially anywhere where heavy equipment is used; the diesel engine is heavily embedded in these infrastructures. The ongoing increase in fuel prices, diminishing petroleum reserves and the environmental concerns caused by burning fossil fuels necessitates finding alternative and renewable sources of fuel. Furthermore a great deal of time, effort and capital would need to be utilised to completely reverse the world's dependency on fossil fuels. There remains therefore a window of time where the diesel engine would remain an important component of energy technology, even with the introduction of new energy sources and technology. Biodiesel holds a promise as an alternative source of fuel for diesel engines (Strayer et al., 1983). Biodiesel can be utilized as a renewable source of energy during this transition phase, and possibly thereafter if large-scale harvesting of solar energy using oil-producing micro-algae becomes commercially viable.

Current biodiesel production methods vary greatly from small scale to large scale, batch and continuous. Fatty Acid Methyl Ester (FAME) biodiesel can be produced by the transesterification of vegetable oil with an alcohol, most commonly methanol. The reaction takes place in the presence of an alkali or acid as well as biological enzymes. Generally the reaction is carried out with an excess of methanol in order to achieve the required conversion of 95%. The excess use of methanol has environmental, economic and energy cost implications. A recent advancement in biodiesel production is the use of reactive distillation (RD). Singh et al. (2004) reported experimental RD that reduced the alcohol to oil feed ratio by 66% i.e. to stoichiometric proportions (three moles of methanol for every one mole of oil).

From the literature it is evident that biodiesel production via RD methods is possible (Singh et al. (2004) and He et al. (2005), (2006), (2007)). The methanol efficiency obtained however is still not as low as stoichiometric. It is understood though that excess alcohol aids in driving the forward reaction. RD combats this as it is able to keep the necessary high alcohol to oil ratio in the reaction zone by recycling the methanol internally, and still keeping the feed ratio

as low as 4:1. Therefore there is still room to improve the process to exactly stoichiometric which is 3:1 alcohol to oil.

1.2 Problem Statement

The starting point for this thesis was an idea for an integrated reactor-separator unit for biodiesel production, making use of reactive distillation principles, declared by von Blottnitz as a potential invention to his employer the University of Cape Town in 2006. The idea was declared in concept form, with a sketch of the equipment and the principles at work, and needed to be turned into a prototype to allow for demonstration of practical use and actual behaviour of the equipment. Once the construction was completed the justification of the design would need to be proven. Focus was placed on methanol efficiency.

1.3 Objectives

The objective of the engineering research reported on and analysed in this thesis was to design, construct and test a novel FAME Biodiesel reactor-separator, making use of reactive distillation. The general construction principles were to be such that the unit could be used by micro-scale producers, as these producers often cause significant human and environmental risk through their methanol usage and wastage. For this reason a desired outcome for the research was to design and build a rig to reach the specified conversion of 95% using very close to or exactly stoichiometric amounts of methanol to oil, so as to avoid methanol handling problems in post-reaction processing.

The thesis objectives are the following:

- To develop a theoretical understanding of the chemical and physical phenomena occurring in reactive distillation of the triglycerides and methoxide in order to produce FAME biodiesel;
- To present the approach to design and proceed with the construction of a prototype to produce biodiesel;
- To report on a series of experimental runs, analyse the results and determine the operability of the prototype using different operating parameters;
- To discover whether the novel configuration is feasible in terms of biodiesel production and to compare it with current industrial norms.

1.4 Methodology

The diagram below represents the projects methodology (Figure 1-1)

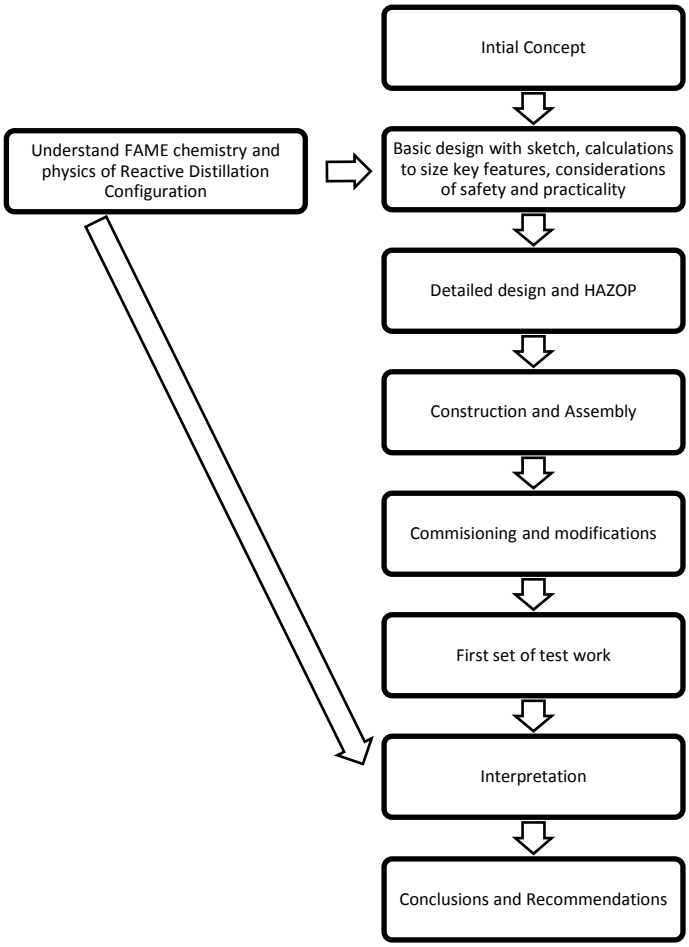

Figure 1-1 Sketch of Methodology

1.5 Scope

The main interest of the research work described in this thesis was to design, construct and commission the novel unit. The experimental runs performed on the test rig were to establish the operability of a few set combinations in the set-up of the rig, relating to the packing height, temperature and primer. The purpose of these experiments was to establish how the

test rig performs. The experimental runs done were limited by time as well as cost constraints.

1.6 Structure of the Thesis

CHAPTER 1: This chapter introduces the thesis as well as providing the reasons for undertaking the project.

CHAPTER 2: This chapter presents the literature relevant to the project. The literature centres on recent findings in the field as well as limitations that may be encountered.

CHAPTER 3: This chapter deals with all the design aspects of the reactor-separator unit; from the conception through to the construction.

CHAPTER 4: This chapter describes the experimental methods. The formulation of the viscosity-conversion chart, initial experimentation and Raoult's Law consideration is also presented in this chapter.

CHAPTER 5: The results from the commissioning, experimental runs, vapour liquid equilibrium and mass balance are presented in this chapter.

CHAPTER 6: An analysis of results as well a discussion on the findings from the experimental runs is offered this chapter.

CHAPTER 7: The final chapter includes conclusions and recommendations drawn on from the entire project. A direction for further work on this project is also presented.

2 Literature Review

2.1 Introduction

This chapter deals with literature gathered on the project at hand. Topics such as transesterification, biodiesel production methods as well sourcing feedstock are unpacked. The literature forms the basis of the project with regard to the gathering of applicable information. This information formed the basis of the direction of the project.

2.2 Transesterification

Transesterification is often used to produce biodiesel. Transesterification is a reaction in which one ester is converted into a different ester. Triglycerides are split during the reaction: the glycerol is removed from the triglyceride and replaced with an alkyl radical from the present alcohol (Canakci & Sanli, 2008). If methanol is the alcohol used, the process acquires the name methanolysis. The overall transesterification of triglyceride with methanol is shown below.

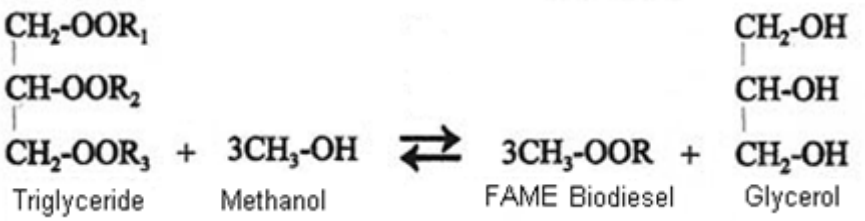

Figure 2-1 Overall transesterification reaction where R`, R_1, R_2 and R_3 represent alkyl groups.

As is evident from Figure 2-1, the molar ratio of alcohol to oil must be 3:1 in order to produce 3 *mol* of biodiesel and 1 *mol* of glycerol. The complete reaction to Fatty Acid Methyl Ester (FAME) biodiesel occurs over 3 consecutive and reversible reactions (Figure 2-2). During the production of FAME, a catalyst is used to increase the rate of reaction. Various acid or base catalysts can be used however in practice the base catalyst is predominant. The reason for this is that using an alkali catalyst (KOH, NaOH) allows the reaction to proceed faster than with an acid catalyst (Formo, 1954)). The first step of the reaction sequence converts triglyceride (TG) to diglyceride (DG) and produces some FAME. In the second step DG is converted to monoglyceride (MG) and some FAME is produced. In the final reversible step, the MG is converted to glycerol and FAME. To drive the forward reaction excess

methanol is added in order to achieve a high conversion. This excess ranges from approximately 1.5 (from general house hold producers) to double the stoichiometric amount. The use of excess methanol is evident both in small and large scale use of transesterification.

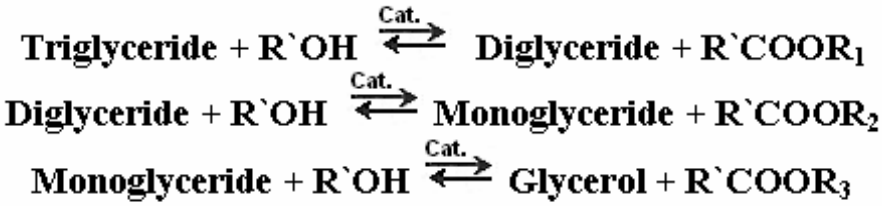

Figure 2-2 The three consecutive reversible reactions where R`, R_1, R_2 and R_3 represent alkyl groups.

2.3 Catalysts

The selection of a catalyst is important in terms of production as well as in terms of feed characteristics. In the production of FAME as mentioned above an alkali catalyst is usually selected. The use of an acid catalyst has limitations but can however come to be useful when considering feedstocks with a high Free Fatty Acid (FFA) content. Use of biological enzymes are also possible but were not considered in the scope of this project.

Free fatty acids are converted into soap when using an alkaline catalyst and essentially consume the catalyst. The soap that forms during saponification is problematic if not removed from the biodiesel product as it can potentially strip the lubrication required in engines. Acid catalysts can be used as they do not form soaps (Freedman et al., 1984). Generally, acid catalysts are not recommended for converting triglycerides to biodiesel as they are too slow (Canakci and Van Gerpen, 1999) although they are good in converting FFAs to esters. Unfortunately a by-product of the conversion of FFAs to esters is water. Water has negative implications in biodiesel production as it inhibits the esterification of the FFAs and the transesterification of the glycerides (Freedman et al., 1984; Canakci and Van Gerpen, 1999). The use of an acid catalyst in this application could therefore only be used as in a type of feed pre-treatment where once reacted; the water could be separated from the reaction zone. Previous work has been performed on placing a pre-treatment unit on a continuous process (Canakci and Van Gerpen, 2001).

Alkali catalysts operate best within the temperature range of 60 – 70 °C, (Fukuda et al., 2001). The use of an alkali catalyst allows the reaction to proceed at an increased rate, more specifically when using sodium hydroxide (Vincente et al., 2004). Essentially however, there is not much difference between using potassium hydroxide (KOH) and sodium hydroxide (NaOH). KOH was found to have a better yield with less saponification; less methyl ester was also found in the glycerol. The reaction performed with NaOH catalysts did however reach completion the fastest (Vincente et al., 2004).

Another factor favouring KOH catalyst is based on considering what happens with the catalyst once it reports in the products. Phosphoric acid can be added at the end of the reaction to the reaction mixture (containing the potassium hydroxide catalyst) to neutralise it resulting in potassium phosphate. This can then be used as fertilizer, recovered as a solid precipitate, (Darnoko & Cheryan, 2000)

The reaction rates increase with an increase in catalyst with regards to the transesterification of sunflower oil. More importantly, the catalyst concentration is very significant for the second and third reactions steps (Vincente et al., 2005). The catalyst concentration utilised by Vincent et al. (2005) for the transesterification of new sunflower oil was 1.5 weight percent of the oil. This value is dependent on the quality of the oil in terms of free fatty acids present. 0.75 weight percent of catalyst can be used for good grade oils as the amount of FFAs are negligible.

2.4 Reaction Kinetics

The kinetics of the transesterification reaction have been studied by Darnoko and Cheryan (2000) and Noureddini and Zhu (1997). Their experiments involved batch processes; however their results cannot be directly compared as they used different catalysts and feedstocks. Some general conclusions however can be drawn from their work with regard to temperature and the reaction mechanisms.

As mentioned above the transesterification reaction takes place over a number of consecutive and reversible steps. More specifically the process follows a second-order consecutive reaction and a fourth-order shunt reaction (Freedman et al., 1986). The variables found to affect the transesterification process are as follows: temperature, type of catalyst, concentration of catalyst, molar feed ratio (alcohol: oil), free fatty acid content and moisture (Noureddini & Zhu, 1997).

The initial stages of the reaction were found to be controlled by the mass transfer of the alcohol to the oil phase (Vincente et al., 2005). The mass transfer affects the reaction rate because of the limited solubility of the methanol in vegetable oils. Mechanical mixing therefore plays an important role because it increases the mass transfer between the two immiscible reactants (Noureddini & Zhu, 1997). The initial stages of the reaction also proceed the fastest (Darnoko and Cheryan, 2000). Biodiesel can be used as co-solvent to ensure the reactants are in a single phase. The advantage of this would also overcome mass balance limitations. The use of co-solvents, in general, in literature is found to decrease reaction time (Lam & Lee, 2010).

The effect of increasing the temperature is limited by the boiling point of methanol ($64.7^{O}C$) in batch reactions. The temperature may also play a role in rapid conversion of the initial stages of the process (Noureddini & Zhu, 1997) as the solubility of the reactants increase (Vincente et al., 2005). Generally at elevated temperatures and mixing levels, the mass transfer controlled region's reaction time was very small (Noureddini & Zhu, 1997, Darnoko and Cheryan, 2000). The second phase of the reaction was confirmed by Noureddini & Zhu, (1997) to be controlled by second order kinetics and mixing was found to have no effect on this phase.

2.5 Reverse Reaction

The transesterification reaction is a reversible reaction and it is therefore important to look at what factors would cause the undesired reverse reaction. Many producers of biodiesel use high concentrations of methanol or run at different pressures and temperatures to drive the

forward reaction. Alternatively, one could remove one of the products of the reaction in order to drive the equilibrium into the forward reaction.

According to Gerpen et al. (2004) the removal of excess methanol in the presence of catalyst will cause the reverse reaction to occur. Methanol recovery generally involves heating the product and boiling off the methanol. As a result to avoid the reverse reaction and recover methanol it is important to first separate the biodiesel and glycerol product (Myint & El-Halwagi, 2008). The first two steps of the transesterification favour the forward reaction. The third and final step however, at high temperature, favours the reverse reaction. The high concentration of the monoglycerides causes the third reaction step to favour the forward direction. This could be problematic at high conversion as the concentration of the monoglycerides would have decreased and heating the product and not removing the glycerol could drive the reverse reaction.

Another interesting point raised by Arrowsmith and Ross (1945), is that if one is processing a feed stream with high FFAs, these FFAs generally form soaps. The soap is said to catalyze the reverse reaction and convert the esters back into FFAs and alcohols. This occurs at temperatures above the region of 140-160^{o}C.

2.6 Current Production Methods

Large and small scale producers of biodiesel follow relatively similar processing. Small scale production refers to farmers, non-commercial producers using waste vegetable oil, etc. while large scale producers opt mainly for a continuous process technology such as the one designed by Lurgi. The Lurgi biodiesel process uses a 2 stage mixer settler unit to produce large quantities of biodiesel on a commercial scale (Figure 2-3).

Generally, of interest to continuous large scale production of biodiesel is optimisation of the production methods with the aim of minimising wastage of methanol. The continuous production methods use many systems of separation in an attempt to recover the unreacted methanol. The unreacted methanol is a result of the excess methanol added to increase the

forward reaction and obtain higher conversions. A novel approach to production has been followed by using reactive distillation. This should permit a decrease in expenditure and improved recovery of methanol.

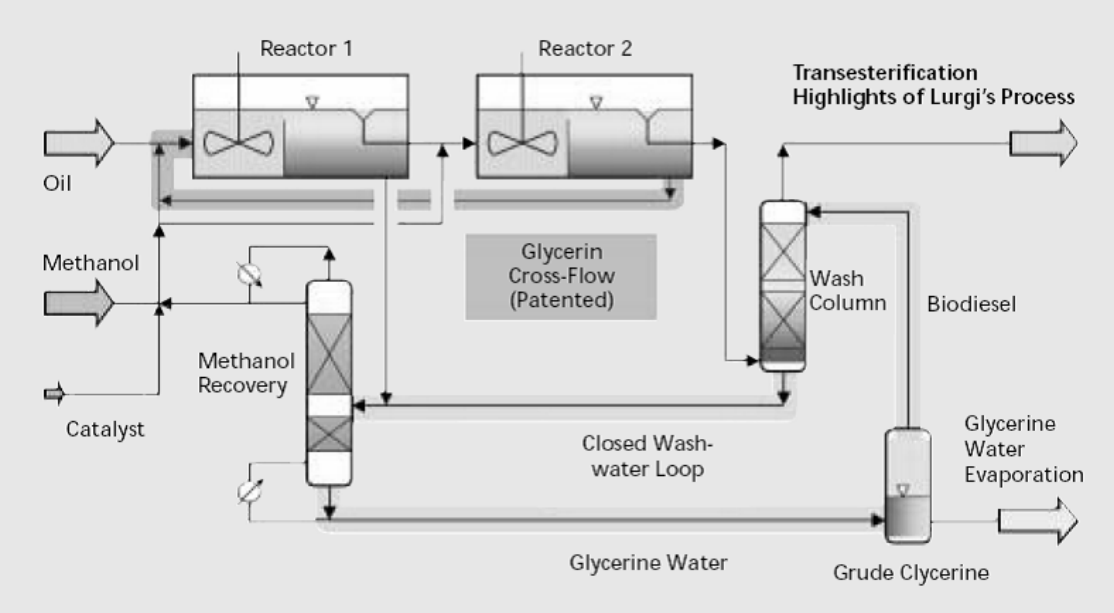

Figure 2-3 Lurgi Biodiesel Production plant (Lurgi, 2005)

Small scale production of biodiesel production is becoming more and more widespread. As a result there are now a vast amount of internet sites offering all the appropriate information on the production of biodiesel. The general procedure is as follows: It involves obtaining the feed materials such as oil, methanol and sodium hydroxide. The feeds are mixed vigorously at the correct concentrations in a tank (batch reactor). The mixing ratios recommended follow generally from the molar ratio used by industrial processes which is 6:1 methanol to oil molar ratio (Fukuda et al., 2001). The product is allowed to settle for an extended period of time so as to separate out the biodiesel from the glycerol. The biodiesel forms as the top layer; it is taken and washed with water. Depending on the grade of the feed oil, the biodiesel product may require to be washed again to remove any remaining catalyst, unreacted methanol or soap. After washing, the biodiesel is allowed to separate out of the water. The biodiesel is then separated and is ready for use.

The main technical concern when using the above processes, small and large scale, is the excess usage of methanol. The amount of methanol used ranges from 30% to 100% above the

stoichiometric amount. The molar ratio of alcohol to used vegetable oil or UVO, (i.e. oil previously used for cooking) has a large effect on ester yield. This is the reason for the large excess of methanol used in production. A further advantage of using a 6:1 alcohol to oil ratio is that the process would be compatible and produces consistent results with a wide range of oil feeds and is therefore used in industrial processes (Fukuda et al., 2001).

The problem with production with a 6:1 molar ratio of methanol is evident in the amount of times the product needs to be washed after production and what is done with the waste water and glycerol containing the unreacted methanol. For large scale continuous production undoubtedly a large portion of the methanol is recycled, however this is performed at additional energy costs for separation. An environmental concern, in addition to that of costs, is raised with regards to the management of the waste water by small scale producers. Small scale producers are unable to remove the excess methanol, if at all, from their waste water. The reason being they do not have the funds, equipment or regard to do so. What is done with the waste water is also important as methanol is toxic to humans.

The glycerol produced also poses an environmental concern. If the vegetable oil feed is clean; the glycerol product can be used to form soap. This is not recommended if the feed stock oil is used cooking oil. If however the purity of the glycerol can be increased to pharmaceutical level, it will allow for further economic benefits as the process would have another product to sell, provided the market allows.

2.6.1 Feedstocks

Feedstocks for producing biodiesel refer to any fat derived from vegetable oil (sunflower oil, soybean oil), or animal sources (e.g. chicken fat, beef tallow). As is evident there are various sources from which one can acquire a feedstock. Industries now opting to buy vegetable oil in large quantities, for the sole purpose of producing biodiesel have caused an increase in demand and hence contributing in increasing the already high food prices (Higham, 2007).

There is also a morality issue raised in that crops should be given as food before being used as oil for fuel. With regard to sources like the jatropha tree which is not a crop, yet biodiesel can be derived from it; there are further arguments that the land used for harvesting the tree should instead be used for crops, to assist in decreasing food prices. Furthermore if an area is deforested in order to grow crops for biodiesel the overall carbon footprint may be greater than not having planted the crops initially. There is a prospect of using oil generated from algae, as a feedstock. This however, can only be considered at a later stage once production of algal oil becomes feasible.

2.7 Reactive Distillation and its Application to Biodiesel Production

Reactive distillation (RD) is the process in which a chemical reaction and product separation are carried out simultaneously in one unit (Coulson and Richardson, 2005). Using reactive distillation is beneficial because of the following reasons: chemical equilibrium restrictions are overcome, as the product is formed it is removed; energy savings can be obtained and capital costs can be reduced as only one vessel is used.

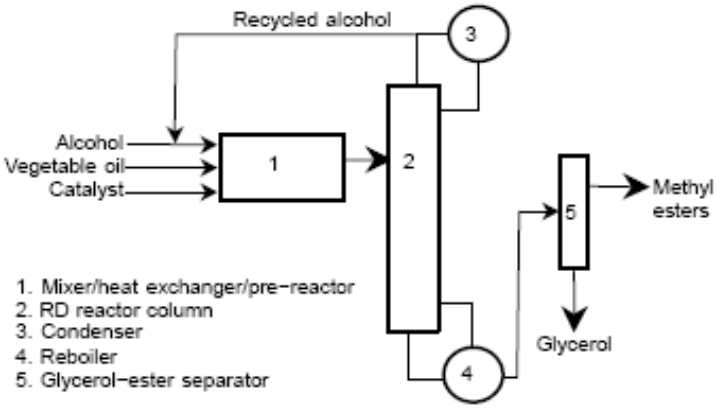

Figure 2-4 Schematic drawing of RD unit (He et al., 2006)

The above experimental setup (Figure 2-4) was used by He et al. (2006). It is a typical set-up used in current biodiesel RD processes. The pre-reactor used is evident in their setup. The data produced from their experiments show final compositions of the components as reported below in Table 2-1 and Table 2-2. From the data it is evident that methanol was found in the

product stream. Although the boiling points of the methanol and the products are very far apart, methanol appears to remain in the product hence decreasing methanol efficiency. From the most efficient runs, in terms of methanol use (Run 3), it is evident that the weight percentage of methanol in the products was 0.9 and the molar ratio was 4:1. A higher molar ratio favours a higher conversion, however as the methanol is in excess it does not completely vaporize from the reboiler at the set temperature (He et al., 2006). The lowest methanol in the product was recorded at a reboiler temperature of 115°C. A run performed by He et al. (2006) with a molar feed ratio of 3:1 (stoichiometric) and the reboiler at 150°C also recorded considerably higher (2.1 weight percent) methanol in the product. This leads to the observation that the solubility of methanol in the products has a large effect on the methanol efficiency as it cannot be entirely used or removed from the product.

Table 2-1 Configurations of RD process setup (He et al., 2006)

		Feed Rate (mL/min)		Temperature (°C)		
Trial	MeOH: Glyceride	Canola Oil	MeOH/ KOH	Pre-reactor	Column	Reboiler
With pre-reactor						
1	3.0:1	6.67	0.8	50	65	150
2	3.5:1	5.67	0.8	50	65	125
3	4.0:1	4.95	0.8	50	65	115
4	4.5:1	4.45	0.8	50	65	110

Table 2-2 Results produced from experimental runs (He et al., 2006)

	Composition (% wt)				MeOH	Conversion	Yield
Trial	ME	MG	DG	TG	(% wt)	(%)	(%)
With pre-reactor							
1	75.6 ±0.88	14.0 ±0.81	6.85 ±0.59	3.53 ±0.51	2.1	78.4 ±0.71	75.3 ±0.87
2	77.3 ±0.61	3.14 ±0.62	7.44 ±0.60	12.1 ±0.14	1.4	78.2 ±0.54	77.0 ±0.60
3	94.8 ±0.08	1.15 ±0.01	2.04 ±0.09	2.00 ±0.04	0.9	95.1 ±0.08	94.4 ±0.08
4	91.5 ±0.05	2.27 ±0.04	3.34 ±0.05	2.88 ±0.05	1.5	92.1 ±0.04	91.1 ±0.05

(Where ME – Methyl Ester, MG- Monoglyceride, DG – Diglyceride, TG – Triglyceride)

The use of RD methods has only recently been reported for biodiesel production (Singh et al., 2004; He et al., 2005, 2006, 2007). In terms of using RD methods for the transesterification reaction, many of the mentioned advantages are applicable. The removal of external recycle streams from separators reduces the waste and therefore waste handling. The removal of methanol which is a reactant from a reversible reaction may in fact be troublesome. If methanol is removed from an area where the forward reaction may still be occurring this may

shift the equilibrium and allow the reverse reaction to occur as previously stated. However if the unreacted methanol is added once again into the reaction zone the forward reaction will be favoured because of the large amounts of excess methanol. He et al. (2006), recorded as high as 15:1 alcohol to methanol. According to batch reactor tests performed (Fukuda et al., 2001), for the catalyst to perform optimally it is important that the column temperature be in the range of 60 – 70 °C. However, as a continuous process is being considered from findings from He et al. (2006), exceeding the 70 °C limit is a prospect.

Table 2-3 Boiling Point data

Component		Boiling Point °C
Used Vegetable Oil		> 200
Methanol		64.7
Glycerol		290
FAME Range	C8	193
	C18	366

Reactive distillation is further feasible when the boiling points of the reactants and products are considered. Their respective boiling points are notably different (Table 2-3). The data for the FAME boiling points were obtained from Yuan et al. (2005). The substance with the lowest boiling, this being the methanol, will boil off from the reboiler and re-enter the reaction zone. Therefore the methanol is now recycled internally. Externally, any methanol that would exit at the condenser can be remixed into the feed stream.

2.7.1 Current RD Biodiesel Production

RD biodiesel production is not yet performed on a large scale. The most suitable information on the process setup in terms of pre-reactor volume, column volume, reboiler volume, residence times as well as configuration is presented by He et al. (2006). This section serves to describe the experimental configuration specific to their work (Figure 2-4). All of the experiments conducted by this group used fresh Canola Oil.

He et al. (2006) used an in-line static mixer which served as a pre-reactor, mixer and heat exchanger, its volume was set at 5mL. The column which had a volume of 21mL was only able to hold up 10mL of liquid. The sum of these volumes (15mL) was regarded by He et al.

as their reactor volume. The base of the column was attached to a 500*ml* flask which formed the reboiler. The amount of liquid at any given time in the reboiler was averaged by He et al. (2006), to be 100*ml*. This was not considered as part of the reactor volume. He et al. (2006) stated that the amount of fluid in the reboiler to the fluid in the column can be significantly reduced on a large-scale unit in comparison to their test rig dimensions as stated above. The residence time therefore stated from the experiment was approximately 3 minutes at a flow rate of 5mL/min (the experiments ran for 300 min to 360 min, needing approximately 60min to reach steady state.

He et al. (2006), based on the fact that the pre-reactor achieved a 30% - 60% conversion of oil, estimated the oil ratio on the column feed tray to be 15:1 – 20:1. The optimum feed ratio was found to be 4:1, because a 3:1 ratio decreased the yield and a 4.5:1 ratio did not increase the yield significantly. The reactor productivity was calculated from the product mixture and found to be 6.6m^3/m^3.h (6 times larger than current batch processes). It is uncertain whether or not there was a reaction occurring in the reboiler but it does seem unlikely as the minimum temperature set was 95^oC and methanol's boiling point is 64.7 °C. A concern here would be; does the methanol in fact evaporate or does it form a new mixture with a higher boiling point?

2.7.2 Pre-Reactor

The function of a pre-reactor is essentially to either mix or heat, or mix and heat reactants before they enter the main reactor unit. The first paper to propose the use of a pre-reactor was published by Singh et al., (2004). Their findings were that a pre-reactor gave better yield when compared to runs performed without a pre-reactor (14% increase in conversion). The reason for this is that the reaction rates were quite high at the beginning of the reaction because of a very efficient mixing regime; hence with the addition of a pre-reactor the bulk of the conversion was performed in the pre-reactor while the balance occurred in the column (He et al., 2005).

The type of pre-reactor also plays an important role as if it is integrated into the process it contributes as mixer/reactor as well as a heat exchanger. The downside however is that it is

now only a crude reactor, and as a result soap was found to form on all runs performed by He et al. (2007). The soap formation increased as the reaction time and catalyst concentration increased. The pre-reactor can be beneficial however it should be looked more as an aid than a means to increase the methanol efficiency.

The paper published by He et al. (2007) focuses solely on understanding the use and performance of a pre-reactor. For their experiments an in-line static mixer was used. The pre-reactor was able to mix the reactants, heat them to a specified temperature and in doing so, as before, perform a large part of the transesterification process. A wide range of results were obtained including a maximum product yield of 84.6%. Soap formation was also recorded and ranged between 2.8% to 10.37%. Even the utilisation of a different catalyst ($KOCH_3$) only slightly reduced soap formation. The same conclusion as mentioned above was drawn in that, the pre-reactor cannot exclusively rectify methanol efficiency.

2.8 Solubility of Methanol in FAME and Glycerol

The distribution of the methanol in the products is important as it affects separation directly. This directly affects costs and energy consumption. As mentioned before, excess methanol is required to drive the reaction to a higher yield. From Singh et al. (2004), the following results were obtained from a higher conversion experimental run: 10% of the methanol was found to leave the column unreacted. 70% of this was found in the glycerol while the balance was found in the biodiesel product. Low residence time or excess methanol, were factors that may have increased the significant amount of methanol in the product stream. It is important to understand however why the methanol is not able to be separated from the products in the reboiler.

In order to establish the composition of the vapour phase generated by the heating of a mixture of substances of known concentration, Raoult's Law may be used if the mixtures in the liquid and the vapour phases are assumed ideal. Raoult's Law states that the partial pressure (vapour phase) of a component in an ideal solution is equal to the product of its mole fraction and its pure component vapour pressure (Sandler, 2006). The sum of partial pressures is equal to the total pressure of the system as described by the equations below

$$x_i P_i^{Vap}(T) = y_i P = P_i$$

Equation 1

And

$$\sum x_i P_i^{Vap}(T) = \sum P_i = P$$

Equation 2

Where: x_i – liquid mole fraction; y_i – vapour mole fraction; $P_i^{Vap}(T)$ – vapour pressure of the species at a specific temperature; P_i – partial pressure of species; P – total pressure of system.

By using Raoult's Law, and assuming complete ideality, one can get a fair understanding of what is expected in a non ideal system from different scenarios.

2.9 Conclusion

The need for biodiesel is justifiable in current society. The means of current production are outdated and inefficient. A novel method of biodiesel production has been proposed which incorporates reactive distillation into the biodiesel production process. The RD method seems to give promising results in terms of conversion of oil to biodiesel. From the literature RD can achieve conversions in the range of 78% to 95%. Limitations to the RD methods may include the solubility of methanol in the product, which was also presented in the literature. A further limitation which might contribute to low conversion is the fact that when using RD methods, an environment which favours the reverse reaction may be created.

3 Design of the Reactive Distillation Prototype

3.1 Introduction

This chapter focuses on the design and construction of the RD unit to produce biodiesel. The initial concept of the test rig is described and discussed. The steps and the procedure followed for the construction of the rig are described in length. The calculations performed, necessary for the design and construction are also presented. The parameters used to control the test rig as well as frustrations with the operability pointing toward further test rig modifications are also discussed.

3.2 Design Concept

A key design aspect of the rig was simplicity. The straightforward design meant that the reactive distillation unit could essentially require minimal costs, minimal energy and minimal controller input. Such features would broaden its application by appealing to small scale as well as large scale producers of biodiesel. A main feature of the rig was to test whether methanol could be added in stoichiometric proportions. The introduction of a reboiler catered for the stoichiometric feed by creating an internal methanol recycle by means of single stage separation. Construction costs could also be reduced by implementing this design as the rig could operate as a continuous process, provided there was sufficient feed, which meant a smaller reactor volume would be required. The fact that the reactor and separator were incorporated into one unit also reduced construction costs.

The initial concept of the rig relied on gravitational flow of the reactants through the unit. The flowrate into the pre-reactor would be controlled by a set of needle valves. The reactants then would flow firstly into a pre-reactor, then, through the packed section of the reactor and finally into the reboiler. The level in the pre-reactor would be controlled by the packing and the viscosity of the reactants. The reboiler level would be controlled by a hydraulic leg. Equilibrium of the flow through the unit was envisioned where flow through the packing would be regulated by the extent of reaction in the pre-reactor as well as the pressure created by the vapourised methanol from the reboiler. Essentially the residence time through the reactor would increase if the viscosity of the reactants was high. With an increase in

conversion of the biodiesel, the viscosity would decrease and flow would therefore increase through the packing. This dynamic system is further explained in Chapter 6.6.

The design for the reactive distillation unit was based on theory and ideas put forward by Von Blottnitz (2006). The design was based on achieving desired residence times in each section of the test unit. The column was structured around three sections, namely: the pre-reactor with a permeable floor (τ = ½ hr); the packed column (τ = ± ¼ hr); and the reboiler (τ = ¼ hr). The figure below (Figure 3-1) is based on the initial concept of the rig

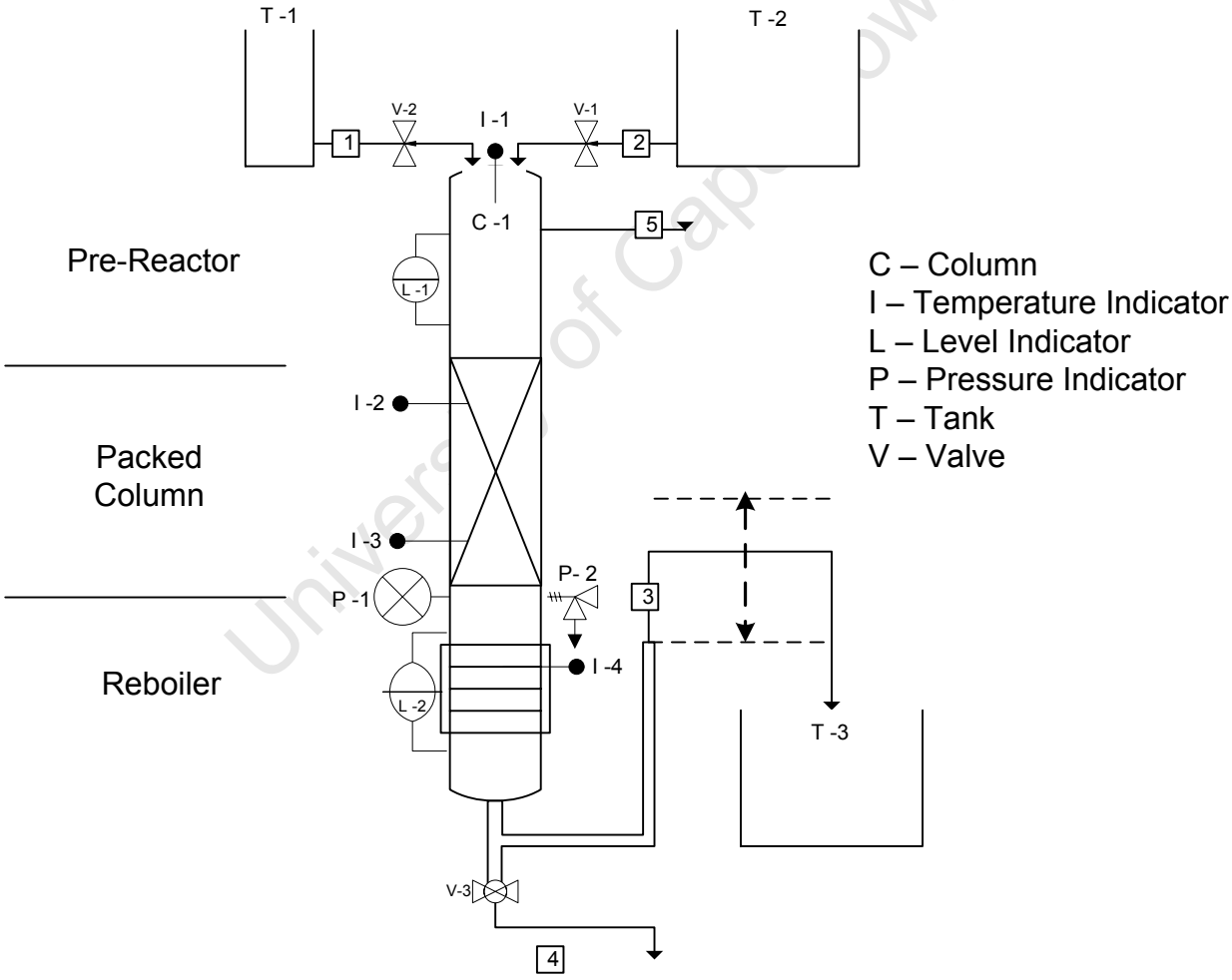

Figure 3-1 PFD of the rig

Figure 3-1 illustrates the feed tanks T-1 and T-2 which feed the test unit. Flow is controlled by V-1 and V-2. Flow first enters into the pre-reactor, which has a level indicator, temperature indicator and an overflow (Stream 5). The liquid then flows through the packing which has two temperature indicators (I-2 and I-3). Finally the liquid flows into the reboiler which is equipped with a pressure gauge and pressure relief valve (P-1 and P-2). The reboiler also has a level indicator and a temperature indicator which is connected to the heating jacket. Flow then enters the adjustable hydraulic leg before entering the product tank (T-3). A more in depth description is presented later in this chapter.

From the design values obtained from literature, the reboiler was designed to be capable of reaching temperatures of up to 150^{o}C. The test rig could also operate under corrosive conditions. As a result the materials of construction used were stainless steel, galvanised steel, glass and Teflon.

The following parameters were designed to be variable and factored into the design of the rig:

- Reboiler Temperature (Continuous from ambient to 150^{o}C)
- Column Height (2 Different Heights)
- Column Packing (Sand packing: Various particle sizes; Specialised packing: 2 types)
- Reboiler Volume (2 Different Volumes)
- Feed Flowrates (Continuous)
- Molar Ratio of oil to methanol

The above mentioned variables would allow for variable operability and the configurational set-up of the test rig. This would be advantageous in structuring test work to obtain optimal performance from the rig.

An approach to safety was also undertaken to ensure the rig did not become a pressure vessel as the unit would be vapourising methanol. Pressure relief, temperature control systems as well as overflows were incorporated in the design. Furthermore, handling concerns of oil or biodiesel at temperatures as high as 150^{o}C was factored into the design. The heating element was insulated and positioned in such a way to ensure the risk of burning out was eliminated. Failsafes, such as a limit on the temperature controller as well as a liquid level controller and

indicator were put in place to ensure that the heating element would never get overloaded. All safety features are further described below in the Detailed Design (Section 3.3).

3.3 Detailed Design

The three different sections of the test unit, namely the pre-reactor, column and reboiler, were attached to each other by flanges (ordered from Waterjet). The flanges allowed for the sections of the test rig to be interchangeable i.e. if the column section needed to be extended. The flanges were made with an oversize OD of 150*mm* to accommodate for easy assembly and disassembly of the rig. The O-rings for the flanges were specially ordered in Teflon as biodiesel would corrode rubber O-rings. The Teflon was also capable of handling high temperatures.

3.3.1 Pre-Reactor

The pre-reactor was fitted with liquid level indicator, an overflow as well as a port for a thermocouple. The level indicator served as a safety feature as well as ensuring that the flowrates into the unit could be controlled. The purpose of the thermocouple was for measuring the temperature of samples (labelled T- I). As samples were taken from the pre-reactor it would be possible to see the extent of conversion obtained at a known temperature. (Figure 3-2)

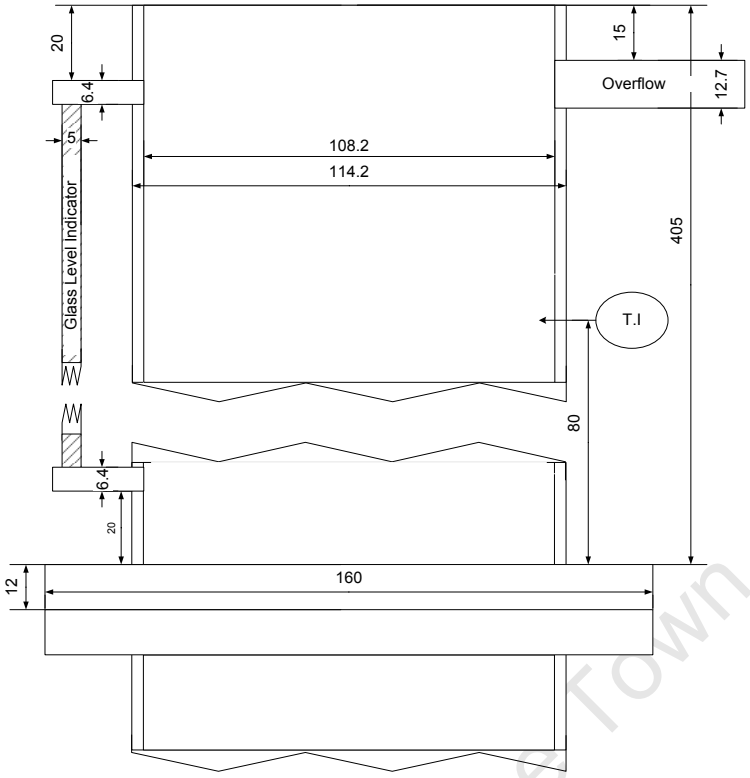

Figure 3-2 Pre-Reactor Diagram

3.3.2 Column

The column was built to contain packing (Figure 3-3). The column's volume was designed assuming a voidage for the packing of 0.4 (Appendix A.3). Two levels were built which could support a tray that carried the packing. Perforated discs were used as trays to support the packing. Wire mesh was also added to the column to contain sand packing. Two ports for thermocouples were placed 50*mm* above each of the two support trays (labelled T. –I). This would give a temperature profile in the column as well as indicating the temperature of the packing which would help determine the heat transfer and the temperature of vapour or liquid in the region.

Beneath the lower tray support, two outlets were made. A manometer was attached to the one exit and the other served as a pressure release system. The manometer was able to give the pressure of the methanol vapour in the column (just beneath the packing). The relief system would ensure that there would be no pressure build up which meant eliminating large safety concerns associated with a pressure vessel. An initially fitted factory pressure relief valve

which proved unreliable replaced with a simple U-tube filled with a known amount of biodiesel to serve as the pressure relief system. The pressure head created by the biodiesel would serve as the maximum allowable pressure before emptying out the contents into the stainless steel bund below.

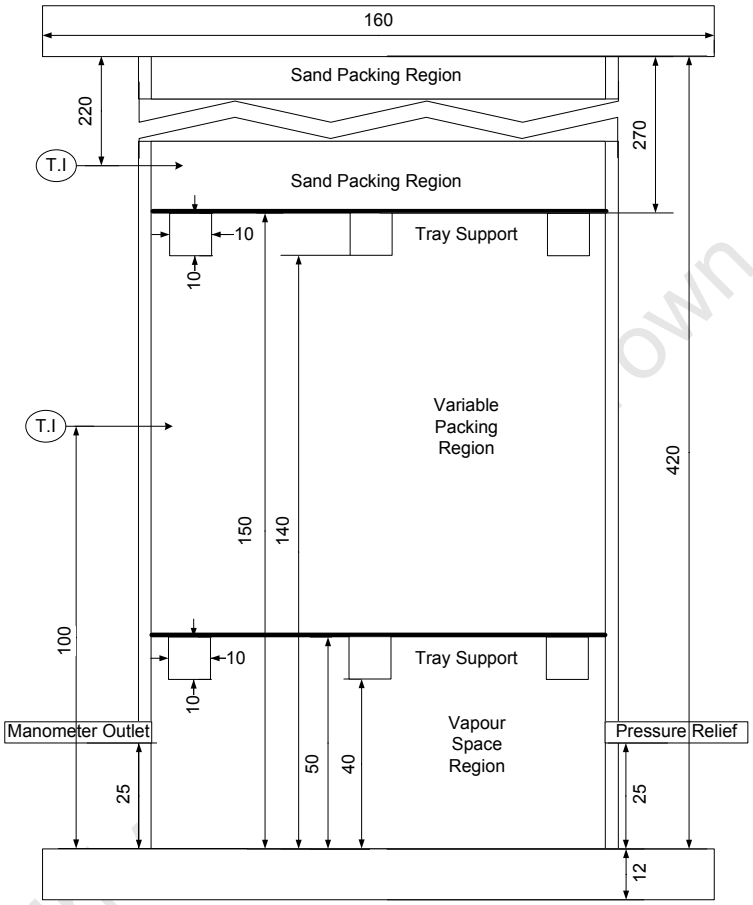

Figure 3-3 Column Diagram

3.3.3 Reboiler

The reboiler was designed to contain an operating volume of 1250ml of liquid (Figure 3-4). To this a safety factor, as with the other operating volumes, was included as well as space for a vapour phase to form. The reboiler was also fitted with a level indicator used to shut off the heating element if there was no liquid in the reboiler. The heating element took the form of a belt which was wrapped around the reboiler. A thermocouple port was also attached to the reboiler which interfaced with a temperature controller. The reboiler was also insulated to ensure that losses to the environment were reduced.

The bottom of the reboiler included a cone which led to a ½ inch tube. This served as the exit pipe of the column. A T-joint was placed at the bottom of the exit tube. A ball valve was attached to the lower end of the T-joint, for draining purposes. The second outlet of the T-joint was attached to more tubing which was opened to the atmosphere acting as a hydraulic leg of a specific height of liquid. The hydraulic leg acted as a level controller. This meant that liquid could remain in the reboiler for a specified time, as the hydraulic leg would create a predetermined reboiler volume. The residence time in the reboiler was therefore dependent on the chosen flow rate as the volume would remain constant. Furthermore the specified height of the exit tubing would ensure that while the rig was operational, the reboiler would not run dry and therefore not cause the heating element to overheat.

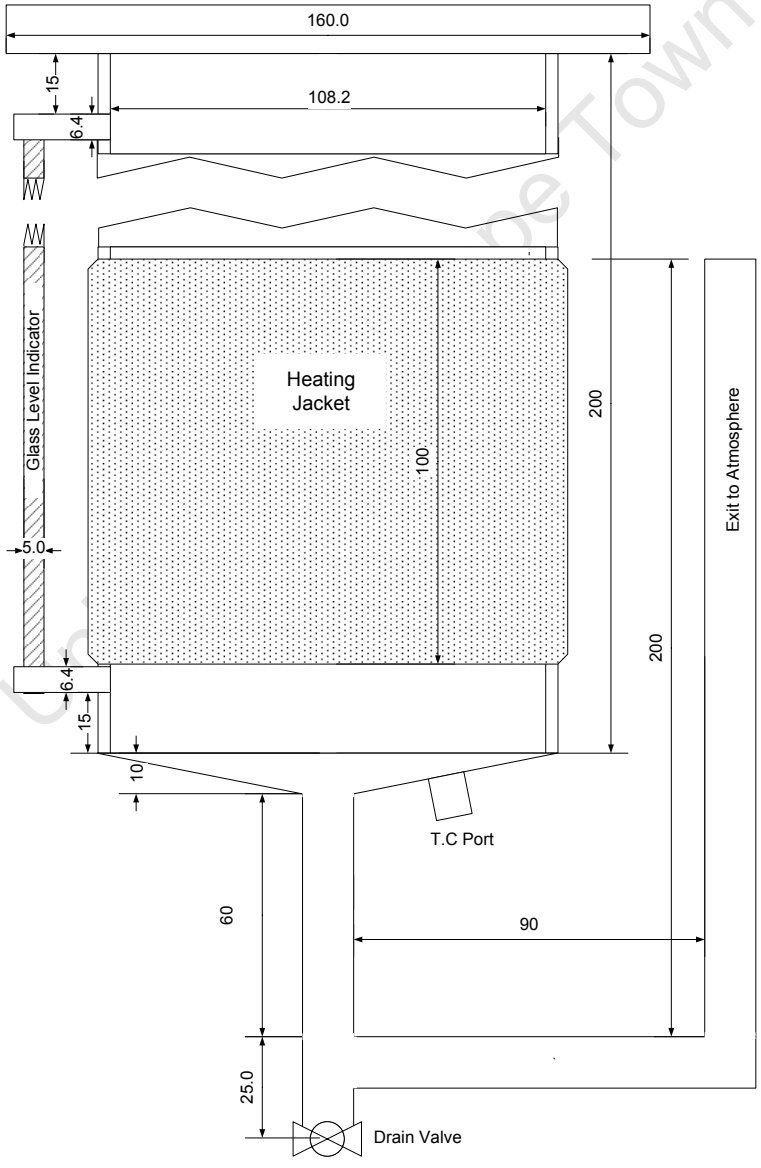

Figure 3-4 Reboiler Diagram

3.3.4 Feed Tanks and Product Tank

Two feed tanks were designed and constructed from stainless steel. The volumes were 50*l* and 5*l* for the vegetable oil, and methanol and KOH mix respectively. The tanks were designed to be long and flat and therefore have a relatively small head of pressure. The feed to the reactor would therefore be controlled by gravity and needle valves attached to the tubing. The small liquid head in the tanks would ensure that as the tanks emptied, their respective flowrates would not very as drastically had the tanks been narrow. The tanks were designed with tapered bottoms to minimise any dead spots and direct the fluid to the exits. Attached to the exit were ¼ inch stainless steel tubing and needle point valves to control the flowrate. The exits to the tubing were positioned above the entrance to the column.

The product tank was also constructed of stainless steel with the capacity of 60*l*. The product tank was cylindrical and was also tapered at the bottom. The exit also featured ¼ inch stainless steel tubing as well as a stainless steel ball valve. This would aid in separation applications.

3.3.5 Control Strategy and Elements

a) Temperature

Temperature control and monitoring was achieved through equipment bought from Unitemp. This included 4 thermocouples, a heating element, a Gefran 600 controller and Gefran 80 Indicator. The J-type thermocouples were all the same dimension to ensure they reached deep enough into the column to obtain a meaningful reading. The temperature control thermocouple was made larger and longer to ensure it was entirely submerged by the liquid in the reboiler. The reboiler was also insulated to minimise losses to the environment.

The heating element chosen was a *2kW* unit to ensure adequate and rapid heating. The element was linked to the Gefran 600 controller. The controller came with an ‘auto-tune’ setting in which the controller is able to set its own constants in order to reach steady state. The controller was said to perform within 1 degree of a given setpoint. The Gefran 80

indicator provided the temperature readouts of the 3 thermocouples placed at different locations on the test rig.

b) Feed

Flow control was in the form of two needle point valves supplied by Control Valve Technology. The valves were attached to ¼ inch tubing which was attached to two overhead tanks. The valves would be set to provide the feed to the reactor.

3.3.6 Packing

a) Sand

The sand used as packing was ordinary beach sand obtained from Camps Bay Beach. The sand was collected from the edges of the beach to ensure minimum foreign objects were present in the sand. Two 20 litre drums where filled with beach sand.

The sand sieved into 4 classes namely: $425\mu m - 500\mu m$, $500\mu m - 600\mu m$, $600\mu m - 710\mu m$ and $710\mu m - 850\mu m$. The finer 2 classes were sieved again to ensure the removal of all particles smaller than $425\mu m$. These small particles needed to be removed as they could pose a problem by blocking the column outlets if they passed through the retaining mesh in the column.

Sea salt was removed from the sand by washing the sand with fresh water. The sand was placed in a drum, water was added which covered the sand and then stirred for approximately 5*mins*. The sand was allowed to settle and the water was then removed. This was repeated several times.

b) Marbles

Marbles of two different diameters were used beneath the sand packing and placed on the second tray support. The diameters of the marbles were 15*mm* and 25*mm*. 33 of the large

diameter marbles were used in conjunction with 145 of the smaller diameter marbles. The marbles would allow for a greater surface area on which the methanol vapour could condense. This would theoretically increase the conversion as the oil would be flowing over the marbles. The marbles would also remain below the reboiler temperature because of their size and the constant flow of reactants entering at ambient temperature. This could therefore ensure condensation. The collective surface area of the marbles was: $1672.9 cm^2$ (Appendix A.1).

c) Specialised Packing

Specialised packing in the form of ceramic Raschig Rings was also used so as to see if an increase in surface area would create a greater conversion relative to using the marbles. 140 Raschig Rings were used with the following dimensions: Height – $17 mm$, OD – $15 mm$, wall thickness – $4 mm$. By exchanging the marbles for the Raschig rings a 23% increase in surface was possible. The total surface are created by the rings was $2172.7 cm^2$ (Appendix A.1).

3.3.7 Supporting Structure

The rig was attached to the centre of a solid moveable frame. Four coasters were attached to the frame for mobility. The two feed tanks were placed above the rig and also held and supported by the solid frame. Provisions on the frame were made for the temperature controller box as well as ease of accessibility in mounting or dismounting the rig form the frame.

A metal bund was placed under the frame, below the test rig, to ensure any spills etc would not affect the surrounding area. The bund also included a drain valve for cleaning purposes. Provisions for the product tank were also made in the structure located within the bund area. The advantage of the solid frame is that the entire test rig was self sufficient, and mobile with the exception of needing an electrical plug point. Furthermore as the frame supported the entire test rig, its dimensions were kept below those of a standard door size to allow for easy movement of the test rig.

3.4 Supporting Calculations

3.4.1 Manometer and Pressure Relief System

The manometer and pressure relief system were designed to ensure the column did not operate as a pressure vessel. A maximum allowable pressure in the vapour space was decided as *1000Pa*. This was used for the design of the pressure relief system and the manometer. The manometer would be able to handle the maximum specified pressure as well as an additional *200Pa*. The liquid used in the manometer was biodiesel. Biodiesel was selected as it would not interfere with the process; furthermore as the diameter of the glass tube was 3*mm* the volume of liquid inserted into the manometer was miniscule in comparison to the volumes of liquid in the process. Therefore in the unlikely event that the manometer liquid entered the process it would have little or no effect.

The density of the biodiesel inserted into the manometer would be measured prior to every run. As the maximum ΔP was known all that was required was the difference in height. From this calculation and the density of the biodiesel assumed to be 880kg/m^3 the design spec of the manometer was found (Appendix A.2). The manometer was designed to able to handle a maximum difference in height of 20*cm*, which was well above the specification calculated value of 14*cm*.

The pressure relief system was an additional manometer with a relief pressure of 1000*Pa* made from glass. When the pressure exceeded this value the contents of the manometer would blow out, into the collection tray, and pressure in the column would decrease. However, it was later found that the performance of the rig stabilised and "blow outs" were reduced when the relief system had minimal liquid and therefore a minimal pressure head. A "blow-out" The minimal liquid in the relief system assisted the test rig to adjust the pressure hence reducing "blow-outs". The relief system and "blow outs" are further discussed on page 36 and page 54 respectively.

The manometer (Figure 3-5) was designed as shown in Appendix A.2. The 50*mm* space in between the U-tube legs was incorporated to accommodate a ruler so observations could be

quantified. The over-extended arm was included so as to reach the column and still allow the manometer to be mounted on the support structure.

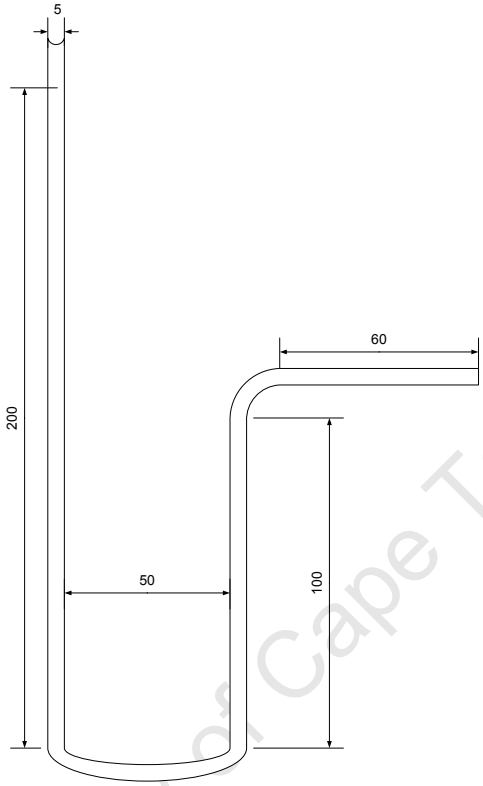

Figure 3-5 Manometer specification (units in *mm*)

3.4.2 Volume of Major Components

The pre-reactor, column and reboiler were constructed using a stainless steel pipe with an ID 108.2*mm* and OD 114.3*mm*. The required volumes for the sections of the reactor were determined by the desired flowrate and residence times. To ensure a 1 hour residence time, a change in liquid flowrate was followed by a change in the liquid volume. The maximum flowrate of 5*l/hr* was used to calculate the volumes. This flowrate was selected to simulate a real application where a rig would be left overnight and by morning a batch of 50*l* of biodiesel (roughly an average car's diesel tank capacity) would be produced. Flowrates were lower than this value and never exceed 5*l/hr*. The appropriate volumes were found to be: Pre-reactor-2500*ml*; column-1250*ml*; reboiler- 1250*ml*. These volumes were increased to accommodate a 10% safety and liquid volume fluctuations (Appendix A.3).

3.4.3 Molecular Weights

Various molecular weights of oil were gathered from the literature (O'Brien, 2004 and Marchetti et al., 2007). A Gas Chromatograph (GC) analysis was also performed on the sunflower oil and represented in Appendix A.4. The advantage of this would be that the composition of the biodiesel (BD) would also be known based on the Fatty Acid content of the oil. The molecular weight of the sunflower oil was 878.54*g/mol* and the molecular weight of FAME biodiesel was 294.19*g.mol*. The molecular weight of the sunflower oil also included a percentage of Free Fatty Acids (FFA). The value of free fatty acids was given by the supplier as 0.06% (Appendix E). In Appendix A.4 is an explanation of the theory used as well as the process followed to calculate the various molecular weights and incorporate them into the mass balance. Molecular weights of the Soaps and FFA were also calculated.

3.4.4 Mass balance

A theoretical mass balance was performed over the process in order to establish oil conversion values. Theory presented in the Literature Review was utilised for the reaction and Mass Balance. The amount of catalyst required was selected to be 7*g of KOH per litre of oil.* This value of catalyst was sufficient to allow for catalyst consumption by the FFAs in the sunflower oils and still function as a catalyst for the conversion of the sunflower oil. The mass balance was presented in a spreadsheet so that it could be altered at any time to suit the actual configuration and performance of the test rig. A process flow diagram was drawn representing the theoretical set up of the test rig (Figure 3-6).

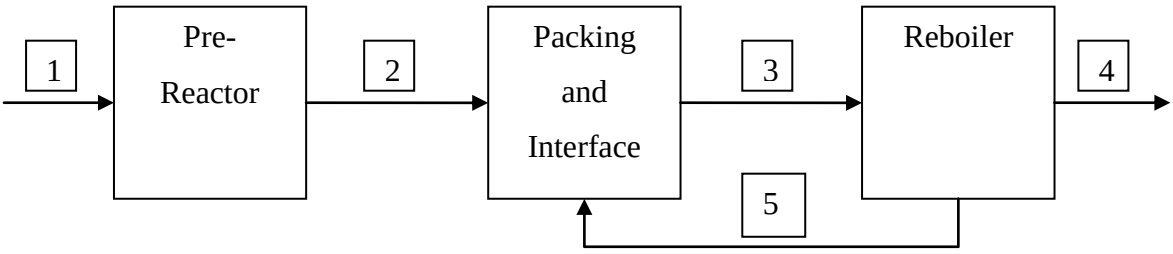

Figure 3-6 Theoretical Process Flow Diagram

Stream 1 is the feed stream. After an assumed conversion in the Pre-reactor, Stream 2 would in theory flow through the sand and into the Packing and methanol vapour interface. During

the packing and interface section there would be further conversion of the sunflower oil (SFO) to FAME. Unreacted methanol in the form of vapour would be supplied by the Reboiler (Stream 5) and rise towards the interface. This would therefore increase the alcohol to oil ratio at the interface and in theory drive the forward reaction. All the methanol vapour would condense and join Stream 3 which would be the liquid entering the Reboiler. Stream 4 is the product stream.

The Mass Balance spreadsheet that Figure 3-6 was based upon can be found in Appendix A.5. In order for the Mass Balance to be carried out, it required the following input values: Volumetric Flow of Oil; FFA percent of the oil; Methanol to Oil Ratio; and the Amount of KOH required. Assumed inputs were Pre-Reactor Conversion; Methanol to Oil Ratio in the Packing section; and the Packing and Interface Conversion. The mass balance operated on the following assumptions: No reaction occurs in the Reboiler; and the Reboiler is able to vaporise all the methanol in the mixture. The final assumption is acceptable as the mass balance offered a rough theoretical guide to the flow regime and could be altered.

The Mass Balance was necessary in order to establish a numerical understanding of the rig as well as include some assumptions that would later be tested when the test rig was run on a continuous basis. The values obtained from the Mass Balance provided a starting point for calculating the flow through the packed bed as applying Raoult's Law Calculations. The below table (Table 3-1) is an indication of the mass balance figures produced by the spreadsheet.

Table 3-1 Mass balance over the rig

MASS		**Stream**	**g/hr**		
	1	**2**	**3**	**4**	**5**
Component					
Methanol	500	250	1441	3	1416
KOH	35	35	35	35	0
TG	4569	2285	228	23	0
FFA	1	0	0	0	0
Glycerol	0	239	455	477	0
Soaps	0	1	1	1	0
Methyl Ester	0	2295	4361	4567	0
Water	0	0	0	0	0
SUM (g/hr)	5105	5105	6521	5105	1416

3.4.5 Packed Bed

The viscosity of biodiesel is approximately ten times less than that of used vegetable oil. The viscosity of the products would play a role in residence time and flowrate through a packed column. The particle size required for the packing was estimated to ensure a total residence time of approximately 60 minutes (the recommended time for transesterification to reach completion, (Noureddini and Zhu, 1997)). A further uncertainty was to what extent the Pre-reactor would convert the sunflower oil to FAME and hence to what extent the viscosity of the liquid had decreased. It was therefore only possible to assume what the flowrate would be as the flow through the column was dependent on the viscosity of the liquid flowing through the column.

For the flow through a packed bed the Karman-Kozeny correlation can be used to describe the pressure gradient across the bed: (Coulson, 1996)

$$u_c = \frac{1}{36K}\frac{e^3}{(1-e)^2}\frac{-\Delta P d^2}{\mu l_{bed}}$$

Equation 3

Where, ΔP, the pressure drop across the bed, l_{bed}, the length of the bed, e, the porosity of the particles, *K*, the Kozeny constant, μ_{fluid}, the viscosity of the fluid, u, the velocity of the fluid, d, the diameter of the particles, ρ_{fluid}, the density of the fluid.

The Karmen-Kozeny correlation (Equation 3) was used in order to establish flow rates and residence times in the column. The equation above can be used under the assumption that flow is laminar, the particles are spherical and the Kozeny constant is equal to 5. The Kozeny constant accounts for the porosity, particle and other factors (Coulson, 1996). Based on literature it was assumed that approximately 50% of the reaction would have occurred before the liquid passed through the sand packing. With this assumption it was possible to obtain the viscosity and density of the liquid. The density and the viscosity of the liquid were calculated

from the Mass Balance spreadsheet using the weighted averages of the four components (Sunflower oil, Methanol, Glycerol and FAME).

The available variables were the liquid level height in the pre-reactor, the viscosity, the voidage, the particle size of the packing and the height of the packing. These values were placed into a spreadsheet where they could be varied and evaluated until the desired liquid residence times were achieved. The above mentioned calculations can be found in Appendix A.6.

The resulting flowrate from the calculation was 5.8*l/hr* with a Pre-reactor Residence time of 40*min* and a Column Residence time of 29*min*. The targets were 30*min* for the Pre-reactor and 25*min* for the Column. This was not seen as a problem as the rig had inherent variability. The Pre-reactor liquid level height which had an operating maximum height of 30*cm* and safety height of 5*cm* before the overflow pipe would come into use. The packing which had a maximum height of 26*cm* could either be decreased or removed completely; alternatively the tray support could be dropped to the level of the second setting and thus increase the packing holding volume by a further 10*cm*. Finally the particle size of the packing could also be altered.

To confirm the predicted flowrates, once the construction and assembly of the rig was completed, the flowrate through the column was checked because of the addition of the various trays and mesh that were added at later stages to keep the packing in place. Additional equipment that was added included the mesh above the sand packing, the mesh below the sand packing, the sand packing tray, the marbles as well as the marble tray.

3.4.6 Heating Element

In order to specify the output of the heating band required a basic energy balance of the Reboiler was performed using the following equation

$$Q = \dot{m} \int_{T_I}^{T_F} C_p \, dT + \dot{m}_{MeOH} \, \Delta H_{vap}$$

Equation 4

Where Q – Energy required (kW); m – Mass flowrate (kg/hr); T – Temperature (K); C_p – Specific heat (kJ/Kg.K)

The equation above was placed into a spreadsheet where the specific heats for methanol, sunflower oil, FAME biodiesel and Glycerol were calculated. The specific heat of the SFO was taken from literature (Santos et al., 2005). An average value was found from the reported data and used for this project's requirements. The specific heat of FAME biodiesel was assumed to be the same as the specific heat of sunflower oil because no reliable data could be found in the literature. For the methanol two specific heats were required, one for the liquid phase and one for the vapour phase as methanol boils at $64.7^{o}C$. A latent heat of vaporisation for methanol was also required. The mass flowrates were taken from the Mass Balance calculations.

The calculations were performed and are reported in Appendix A.7. The maximum heating rate was determined to be $0.61kW$. This was done under the assumption that the rig would need to heat a liquid at a flowrate of $5l/hr$ from room temperature to $180^{o}C$. The heating band however was ordered with a $2kW$ heating element to ensure that the rig would heat and reach steady state rapidly. It was also beneficial to order a more powerful heating band to allow for discrepancies in the assumptions made as well as ensuring that if the reboiler volume was altered the heating band would be capable of performing adequately. An advanced controller was purchased with the heating band to ensure smooth performance from the equipment.

3.5 Modifications

Once the rig was assembled and pre-commissioned, a set of six commissioning runs were performed to establish the operability of the rig. These runs are presented in Chapter 4.2, Chapter 5.2, and in Appendix C.1. It was during this stage that the configuration of the test rig was altered to allow for improved biodiesel conversion, and functionality. The modifications made are explained below:

3.5.1 Feed Tanks

The objective of the feed tanks was to use gravity to supply the feed to the reactor. The tanks were designed to have a small head so that the flow would not vary greatly with time. The tanks had a conical bottom to allow drainage to the tubing that fed the test rig. The feed tanks however proved problematic in terms of flow as the viscosity of the oil used in the initial runs varied. The feed tanks did not help create a steady state as the flow from both tanks was constantly decreasing as the head in the tanks decreased.

In order to maximise control and reduce variability the feed tanks were abandoned for two *Masterflex* Variable Speed Peristaltic Pumps. The pumps were set up to feed oil and the methoxide mix respectively. The addition the pumps also simplified the shut-down procedure as reactants were pumped as required. Post run measurements could also be readily read off the new feed containers which were graded.

3.5.2 Overhead Stirrer and Primer

An overhead stirrer was incorporated to cope with the immiscibility problems of the oil and the alcohol. Initially the two feed streams were positioned to merely pour into the Pre-reactor. This was first altered by placing the feed stream into one Y-connector; this still did not give satisfactory results. An overhead stirrer with variable speed setting was attached to the top of the support structure of the rig. The impeller speed was set at a constant rate for the duration of the experiments. The stirrer was able to overcome the immiscibility problems as well as promote the forward reaction by reducing mass transfer limitations.

A further modification introduced to overcome immiscibility problems was the feeding of biodiesel primer. The biodiesel primer was added to the standard primer consisting of methanol (with the catalyst already dissolved) and sunflower oil. The biodiesel allowed for sunflower oil and methanol to be completely miscible.

3.5.3 Sand Packing

The sand packing used for all the runs was the $710\mu m - 850\mu m$ range. This was not altered as the flowrate and liquid level proved to be a challenging set-up to control. This is further described in the Results Chapter.

3.5.4 Condenser

A condenser was required to ensure that there was minimal methanol escaping from the rig from the modified outlet and no "blow-outs" occurred. The condenser was only utilised on specific runs. A silicon tube linked the test rig to the condenser. At the outlet of the condenser there was a measuring cylinder to quantify the amount of methanol that escaped.

3.6 Conclusion

The figure below (Figure 3-7) is a photo of the overall rig. The rig was designed and constructed to specification and was able to alter specific parameters that would affect conversion. The six commissioning runs were essential in verifying a path on which to proceed for further experiments although their conversion was not necessarily as high as was previously anticipated. The calculations performed in this chapter were based on a theoretical interpretation of how the test rig should perform. The design and construction of the unit that can produce biodiesel was successful.

Figure 3-7 Photo taken of RD Unit

4 Experimental Investigation: Methods and Plan

4.1 Introduction

This chapter focuses on the experimental test rig runs which followed the commissioning runs. The commissioning runs were based on initial operability and understanding of the rig and assisted in creating a rigorous experimental procedure used in the experimental runs. A total of six commissioning runs were performed. The experimental runs are explained in this chapter.

This chapter also includes methods that facilitated data capturing as well as a method of data analysis which was established to complement findings in determining the operability of the unit. Stand alone batch experiments were performed not using the test rig to allow for a comparison to be made between the test rig experimental results and the simplistic batch method of biodiesel production and therefore determine the feasibility of the test rig.

4.2 Commissioning Runs

The aim of the commissioning runs was to establish the basic operability of the rig. This meant the determination of the region of operability of the unit which ensures reproducible results. The test rig was therefore run on theoretical assumptions until the above mentioned factors were unpacked.

The findings of the commissioning runs are presented in the next Chapter 5.2. These runs helped refine the experimental method and focus on specific variables that were found to have the greatest effect on biodiesel conversion. The commissioning runs also pointed to modifications to be performed on the rig (see Chapter 3.5).

4.3 Experimental Test Rig Runs

The experimental runs followed on from the findings of the commissioning runs. In the commissioning runs certain variables became prominent while others remained irrelevant to the conversion capability of the rig. The liquid level height could be better maintained by

varying the biodiesel concentration in the test rig primer; as a result the conversion became more stable and reproducible. The modified test rig primer allowed for an easier control of the liquid level. In addition factors that were found to be relevant to biodiesel conversion were the reboiler temperature, and the surface area of the packing.

As a result the experimental tests focused primarily on the test rig reboiler temperature, the surface area of the packing and the composition of the test rig primer. A total of fourteen experimental runs were carried out as part of the experimental phase. Ten tests runs centred on varying the reboiler temperature. The temperatures used were 70^{o}C, 90^{o}C, 110^{o}C and 140^{o}C. The remaining four runs involved the variation of the packing between marbles and Raschig rings and changes in composition of the primer. Focus was also placed on the molar ratio of the oil and methanol as well as the pre-reactor residence time.

4.4 Procedure of experimental test runs

4.4.1 Feed stock

The project was essentially intended to run on used vegetable oil (UVO) in order to avoid the previously mentioned social problems. Using UVO has process implications in that consistency of the feed oil varies. When obtaining used oil from various fast food outlets it is uncertain what type of oil the respective outlet is using. Different oils are used to fry potatoes as opposed to chicken or fish. A further problem is debris from the cooked food in oil and water contamination. Certain oils from the food (fish oil), could affect the process and reproducibility of the experiments. Although particles may be filtered out of the oil this is not an easy process. The excessive use of the cooking oil also plays a role in biodiesel yield. "Abused" oil will yield less biodiesel as prolonged heat decomposes the oil.

In order to obtain comparable results, certain external influences such as using UVO were required to be eliminated. It was therefore decided that fresh sunflower oil would be used to produce consistent results. Once meaningful and desired results were obtained a switch to UVO could be more applicable. Sunflower oil is costly but easily attainable from local suppliers: Biodiesel Centre and Supa Oils.

The characteristics of the oil were obtained from the supplier. Focus was placed on Free Fatty Acid (FFA), moisture content as well as saponification value all of which have a direct effect on biodiesel yield. The composition of sunflower oil was found from literature to contain 4.3% Palmitic, 4.7% Stearic, 60.4% Oleic and 30.6% Linoleic, Fatty Acids (O'Brien, 2004). The composition of the sunflower oil used was determined from a GC analysis (Appendix A.4) and presented on the table (Table 4-1) below. The specification sheet obtained from the supplier is available in Appendix E

Table 4-1 Composition of sunflower oil used

Fatty Acid				Composition
			MW	GC
Myristic	C14:0	$C_{14}H_{28}O_2$	228.378	0
Palmitic	C16:0	$C_{16}H_{32}O_2$	256.432	0.06083
Palmitoleic	C16:1	$C_{16}H_{30}O_2$	254.416	0
Stearic	C18:0	$C_{18}H_{36}O_2$	284.486	0.05083
Oleic	C18:1	$C_{18}H_{34}O_2$	282.47	0.24192
Linoleic	C18:2	$C_{18}H_{32}O_2$	280.454	0.63756
Linolenic	C18:3	$C_{18}H_{30}O_2$	278.438	0
Arachidic	C20:1	$C_{20}H_{40}O_2$	312.54	0.00245
Gadoleic	C22:1	$C_{22}H_{46}O_2$	342.61	0.00641
Behenic	C22:2	$C_{22}H_{44}O_2$	340.594	0
Other				0

Laboratory grade methanol and Potassium Hydroxide were also purchased and utilised for the experiments.

4.4.2 Start-up

The start-up procedure was consistent with all experimental test rig runs performed.

The mix of methanol and KOH (methoxide) was prepared by mixing 2*l* of methanol and the pre-specified amount of KOH. The amount of KOH predominantly used in the methoxide for the runs was 0.76 weight percent of the oil. This was left to mix with a magnetic stirrer for approximately 45*mins*.

The rig needed to be primed in order to reach steady state rapidly. This was achieved by placing specified quantities of sunflower oil, methanol and biodiesel into the rig as well as by preparing a primer mix. The concentration of the various primers remained constant for the bulk of the experimental runs and given below:

3 glass beakers were set aside with:

Beaker 1 Reboiler → 1250*ml* of biodiesel
Beaker 2 Column → 1000*ml* of biodiesel
Beaker 3 Pre-Reactor → 1000*ml* biodiesel with 1000*ml* of sunflower oil and 126*ml* of methoxide.

The height of the hydraulic leg which determined the level in the re-boiler was set and Beaker 1 was poured in to the test rig from the top of the test unit. Time was given for the biodiesel to filter through the column. Once the level in the reboiler was higher than the height of the heating jacket the main power to the rig was switched on. The desired reboiler temperature of the run was inserted into the controller. The rig was then left so that the reboiler could reach the desired temperature. 4*g* of methanol were added to the reboiler to ensure the vapour in the void (area between the packing and the liquid in the reboiler) was only full of methanol vapour. 4*g* was calculated as the amount of methanol needed to fill the vapour space. This amount of methanol would serve as a primer for the internal methanol recycle.

While the rig was heating up, the flowrates of the feed pumps were tested individually. The methoxide feed was tested and adjusted first to the specified flowrate. The methoxide was added first as it had a low flowrate and was therefore very sensitive to adjustment. The sunflower oil line was then tested and matched to be within the stoichiometric ratio of the methoxide line. The bucket and stopwatch method was used to measure the respective flowrates. Two graded feed buckets (sunflower oil and methoxide) were then used as the feeding tanks which supplied the feed to the test rig via the two respective pumps. The level of feedstock liquid in each feed bucket was recorded before and after the conclusion of the experimental test run.

Once the reboiler temperature reached its set point Beaker 2 was added to the column. Once the biodiesel from Beaker 2 flowed through the pre-reactor and filled the sand bed below (this was gauged by using the liquid level indicator on the pre-reactor), Beaker 3 was added

(Pre-reactor primer mix). The level was allowed to drop to 200*mm* at which point the feed pumps were activated and the run was started.

4.4.3 Sampling

4.4.3.1 Sample Preparation

In order to standardise the sampling process all samples were prepared in the same manner. 45*ml* plastic sample containers were used. A solution of acetic acid and distilled water (3*ml* of acetic acid and 17*ml* of water) was placed in each container. The calculation of the amount of acetic acid added is given in Appendix B.1. During the experimental test runs a 20*ml* oil sample obtained from the test rig was added to the sample container. Oil samples were taken from both the pre-reactor and the reboiler (test rig product exit pipe).

The water in the sample container was necessary to absorb any unreacted methanol and/or glycerol from the sample. The volume of the acetic acid and water mix and the volume of the oil sample were the same (20*ml*) in order to maximise the amount of methanol removed. Mixing of the sample played a bigger role in methanol removal from the oil sample. The acetic acid was added to neutralise the reaction by reacting with all the KOH catalyst. The neutralisation reaction is described as follows

$$HCH_3COO + KOH \rightarrow KC_2H_3O_2 + H_2O$$

The neutralisation of the KOH ensured the forward transesterification reaction does not occur while the sample was left to settle prior to being placed through the viscometer.

Once the oil sample was placed in the sample container it was shaken and mixed. It was important not to mix the sample too much as an emulsion would form. The emulsion would render the sample unusable. After mixing, the samples were allowed to rest for 24-26*hours* to ensure complete separation and settling of the water and acetic acid solution from the oil phase.

Once the samples had settled they were placed through the viscometer to obtain a time reading, necessary for determining the viscosity of the sample. As is shown below the viscosity was used to calculate the conversion or amount of biodiesel in the sample. The figure below (Figure 4-1) is a picture of BS/U-tube D-type viscometer used for all viscosity analyses.

Figure 4-1 Viscometer used for analysis of all biodiesel samples

4.4.3.2 Sample Taking

Prior to the experimental runs a minimum of 20 sample containers with the acetic acid neutralisation solution were prepared. Dependant on the nature of the run more sample containers were prepared when required. The samples were labelled for the pre-reactor and the reboiler respectively. Samples were taken every 20*mins*.

The samples from the pre-reactor were obtained using a 20*ml* pipette inserted from the top of the test rig column. The stirrer would be shut off and the sample taken and placed in to the container. Once the oil sample was placed in the container, the sample container was lightly shaken 3-4 times to ensure good mixing and neutralisation of KOH. Caution was taken with mixing so as not to cause an emulsification. The samples from the reboiler were taken from the test rig exit pipe. The sample container was placed under the exit flow pipe and allowed to fill to the specified mark on the container (20*ml*). The same mixing routine was used as with the pre-reactor samples.

In total 9 sample containers were used for the pre-reactor and reboiler respectively. The remaining two sample containers were used to sample the reboiler product bucket at 120*mins* and 180*mins*.

4.4.4 Data Recording

The temperatures of the reboiler, packing, sand bed and pre-reactor were recorded every time a sample was taken (every 20*mins*). The liquid level height in the pre-reactor was also recorded. Notes were also made during the duration of the run, stating improvements or observations that could benefit future runs.

All captured data was placed onto a template and later entered into a spreadsheet for processing.

4.4.5 Operation and Shut Down

During the experimental test runs all required operating variables were monitored. Most importantly the liquid level height in the pre-reactor needed to be maintained and not drop below 200*mm.* The decreasing levels of the sunflower oil and methoxide feed buckets were checked to ensure flow remained stoichiometric.

The shut down procedure was performed once the final sample was taken. The Temperature controller was set to 0^{o}C and then the entire heating box switched off. The feed pumps and stirrer were then switched off. A bucket was placed under the reboiler drain valve at the bottom of the column and the column was allowed to empty overnight. The remainder of the feed of methoxide and sunflower oil were placed into two separate storage containers.

4.5 Method for Deriving Conversion from Viscosity

One of the main aims of the project was to achieve a high conversion of vegetable oil to biodiesel. The analysis of the product proved to be challenging as GC analysis at the University of Cape Town could not quantify the amount of triglyceride or biodiesel in the

mixture, it could only quantify the amount of Fatty Acids present. It was therefore decided to estimate the conversion of the biodiesel based on the viscosity of the samples measured by the viscometer.

One of the ASTM standards for biodiesel is kinematic viscosity of a sample which needs to be in the region of 1.9 – 6 mm^2/s at 40^{o}C. Testing the viscosity of the product proved to be the most attainable and consistent approach in inferring biodiesel conversion. The viscosity test would prove sufficient for the scope of the project. The reasons being a) only "clean" sunflower oil was used which meant FFA's were minimal; b) laboratory grade KOH and Methanol were also used which meant all reactants were of high quality; c) As the FFA content was known to be low there was no soap formation; d) No water was used in the process or entered the process through reaction.

4.5.1 Viscosity Chart

4.5.1.1 Conversion Chart

The viscosity of the sunflower oil was measured in the laboratory at UCT using the BS/U-tube D-type viscometer shown above (Figure 4-1). The tests were performed at room temperature (26^{o}C) and three viscosity-times for each sample were recorded. A constant temperature bath was also set-up to measure the viscosity of the samples at 40^{o}C. In order to obtain the viscosity from the recorded viscosity-times of the samples, the following equation was used

$$\nu = C \text{ x } t$$

Equation 5

Where $\boldsymbol{\nu}$ - Kinematic viscosity (mm^2/s), $\boldsymbol{C}$ – Given constant ((mm^2/s)/s), $\boldsymbol{t}$ – Time (s)

The constant for 40^{o}C was given by the supplier of the viscometer as **0.10384(mm^2/s)/s**. The viscometer constant for 26^{o}C was calculated from an equation given by the supplier and found to be **0.10348(mm^2/s)/s** (Appendix B.2).

The conversion chart was established using the viscosity of sunflower oil methyl ester at room temperature and viscosity of sunflower oil at room temperature. These two points were taken as 0% conversion, which would have the same viscosity as unreacted sunflower oil, and 100% conversion would have the same viscosity as the sunflower oil biodiesel. These two values were the beginning and end points of the conversion chart respectively.

A batch of sunflower oil biodiesel was made. The weights of the reactants and products were recorded so that an accurate mass balance could be established. From the mass balance the percent conversion was deduced as 98% completion of the transesterification reaction (Appendix B.5). The biodiesel produced was done in order to establish the viscosity of sunflower oil biodiesel at room temperature and at 40^{o}C; as well as change in viscosity that occurred between the above two end points.

An experiment was conducted, in which sunflower oil biodiesel and sunflower oil were mixed in varying volume percentages. Six different samples of sunflower oil and sunflower oil biodiesel were made. The mixtures ranged from 0% sunflower oil to 100% sunflower oil, in 20% increments until 100% sunflower oil. Each of these mixtures was tested for their respective viscosities at room temperature (26^{o}C) and at 40^{o}C. Three viscosity tests were performed per sample.

The tables below, Table 4-2 and Table 4-3, illustrate the recorded times as well as the corresponding viscosities obtained by multiplying the recorded times with viscometer's constant.

Table 4-2 Kinematic Viscosities obtained at Room Temperature

Temp	26°C						Constant	0.103483	(mm²/s)/s
Mixture			Mass	Density	Time (s)				
% BD	BD (ml)	SFO (ml)	g/10ml	g/ml	1	2	3	Avg.	*v* (mm²/s)
0	0	40	9.15	0.915	617.32	652.5	635.28	635.0	65.7
19.6	7.84	32.16	9.0925	0.90925	372.5	386.69	389.88	383.0	39.6
39.2	15.68	24.32	8.96	0.896	231.47	230.12	238.04	233.2	24.1
58.8	23.52	16.48	8.885	0.8885	148.09	149.12	148.41	148.5	15.4
78.4	31.36	8.64	8.84	0.884	98.28	98.35	98.25	98.3	10.2
98	39.2	0.8	8.75	0.875	58.31	59.75	59.65	59.2	6.1

Table 4-3 Viscosities obtained at 40°C

Temp	40°C						Constant	0.10384	(mm²/s)/s
Mixture			Mass	Density	Time (s)				
% BD	BD (ml)	SFO (ml)	g/10ml	g/ml	1	2	3	Avg.	*v* (mm²/s)
0	0	40	9.1	0.91	339.5	355.62	356.5	350.5	36.4
19.6	7.84	32.16	9.03	0.903	226.94	230.22	242.38	233.2	24.2
39.2	15.68	24.32	8.89	0.889	146.53	148.93	143.56	146.3	15.2
58.8	23.52	16.48	8.83	0.883	96	99.85	101.35	99.1	10.3
78.4	31.36	8.64	8.79	0.879	67.84	68.56	69.35	68.6	7.1
98	39.2	0.8	8.67	0.867	44.84	44.96	45.53	45.1	4.7

The same D-type viscometer and constant temperature bath were used for the entire experiment. As the above analysis did not in fact measure conversion but a viscosity based on a volume composition of the mixture it was important to convert the volume percentages to values that would signify conversion. This was successfully done in Appendix B.3.

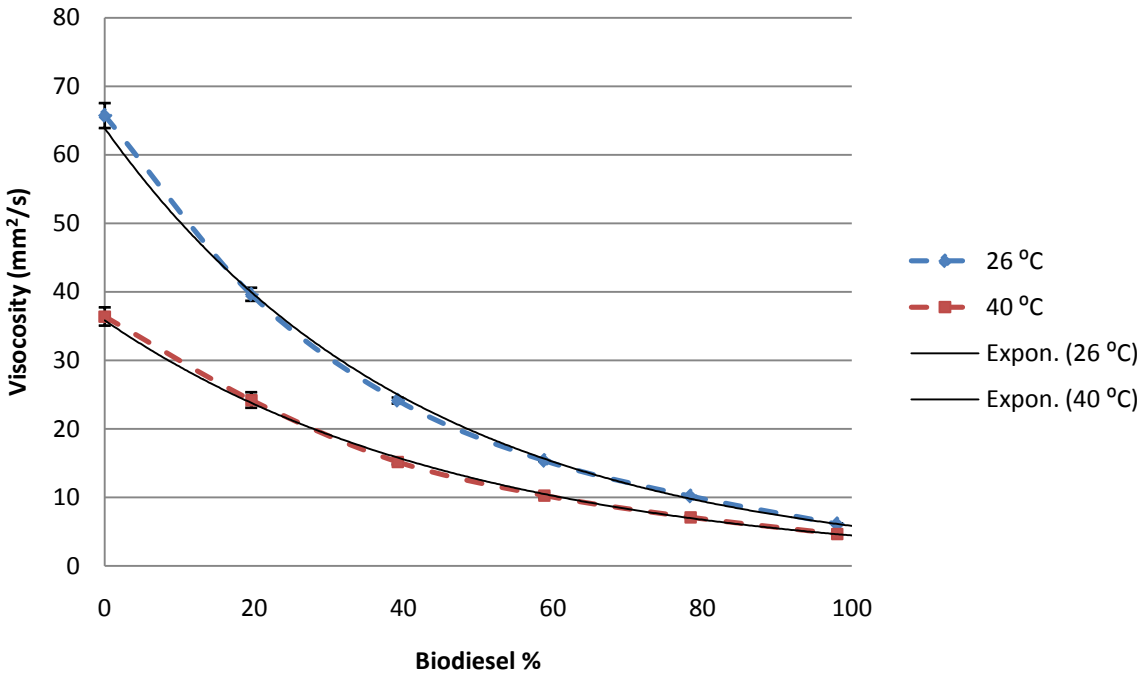

Figure 4-2 Conversion Chart established from experimental data

Having proved that the volume percent and conversion are interchangeable in Appendix B.3, the above graph (Figure 4-2) was plotted. The figure above illustrates the resultant graphs obtained at the 2 different temperatures for the varying mixtures. The densities of the mixtures were also recorded.

The viscosity of the sunflower oil biodiesel recorded was 4.7mm^2/s. This value was within specification of ASTM standards for biodiesel. This value also matched closely to the literature value of 4.2*mm*^{2}*/s*. The error bars inserted in Figure 4-2 were found to increase with increasing length of recorded viscosity times. The error bars were drawn with a 98% confidence interval. This did not pose a problem for using the viscometer at later stages as the higher the conversion of the process the more accurately the viscometer would read.

Trend lines from Excel were fitted to the data points and graphs were derived. The trend lines, as is evident fall within the error bars. The following equations are from the Excel trend lines and would later be used to predict the viscosity of sunflower oil and sunflower oil biodiesel.

For ambient temperature (26^{o}C)

$$y = 63.85^{-0.02x}$$

Equation 6

For 40^{o}C

$$y = 35.84^{-0.02x}$$

Equation 7

Where ***y*** – Kinematic viscosity (mm^2/s)**,** ***x*** – Biodiesel conversion (%)

For a given viscosity, measured in BS/U-tube viscometer, a percentage of biodiesel conversion, at ambient temperature and/or at 40^{o}C, could now be given using the above graphs, Figure 4-2 or the generated equations, namely Equation 6 and Equation 7 respectively.

4.6 Stoichiometric Batch Reactions

Several batch reactions were performed in order to verify the possible limits or goal points achievable by stoichiometric reaction as well as to verify the viscosity conversion chart. The batch reactions were performed using 1*l* of sunflower oil, 126*ml* of methanol and 7*g* of KOH. A 2*l* sealable glass beaker was used as the reaction vessel together with a magnetic stirrer.

4.6.1 Maximum Conversion

This batch reaction was performed under ideal conditions. The sunflower oil was preheated and then added to the methanol and KOH mixture. The entire beaker was placed on the magnetic stirrer with the lid sealed. A constant temperature of 40^{o}C was maintained as well as a constant mixing rate. The reaction was allowed to run for 2*hrs*.

Weights of the reactants were taken before and after the run. The glycerol produced was separated from the FAME biodiesel and placed in an open beaker. The volume and the weight of the glycerol were recorded. Similarly, the volume and weight of the sample of the FAME biodiesel were also recorded as well as placing the FAME in an open beaker. The two

beakers were placed on a heating plate and left overnight on low heat. The purpose of this was to determine the amount of unreacted methanol in the FAME biodiesel and the glycerol phase respectively. This would aid in producing an accurate mass balance and percent conversion of FAME.

The below table, Table 4-4, represents the mass balance conducted over one of the two ideal stoichiometric batches performed.

Table 4-4 Stoichiometric Batch Mass Balances

Conversion	**80 %**						
Substance		**In**			**Out**		
	Density	Vol (ml)	Mass (g)	Mol	Vol (ml)	Mass (g)	Mol
TG	0.913	1000	912.7	1.036	196	178.9	0.203
Methanol	0.792	126	99.8	3.114	25	19.7	0.614
KOH			11.0			11.0	
Glycerol	1.126		-	-	68	76.8	0.833
SFOBD	0.868		-	-	849	737.1	2.500
Total		1126	1023.4	4.150	1138	1023.4	4.150

From the two heated samples mentioned above the amount of unreacted methanol was found to be 19.67*g*. The calculations are presented in Appendix B.4. The amount of reacted methanol allowed for a conversion of 80 % to FAME Biodiesel.

4.6.2 Conversion Verification

A sample was taken from the above mentioned batch reaction. The sample was put through the BS/U-tube viscometer. The respective conversion was calculated using the Viscosity Conversion Chart.

A second stoichiometric batch was also performed following the identical procedure of the above mentioned first batch, and the experiment was duplicated. The samples from the first

and second stoichiometric batch were measured three times through the viscometer to ensure consistency. The following table, Table 4-5 , represents the results.

Table 4-5 Proof of Consistency of Viscosity Chart Conversion

Batch	**1**			**Batch**	**2**	
Sample				**Sample**		
Time (s)	**Visc. (mm^2/s)**	**Conv. (%)**		**Time (s)**	**Visc. (mm^2/s)**	**Conv. (%)**
99.47	10.29	79.35		96.65	10	80.6
95.44	9.88	81.15		96.1	9.94	80.85
97.16	10.05	80.37		92.75	9.6	82.39
	Average	80.29			Average	81.28
Final Conv.	80.78	%				

The final conversion was taken from averaging the (averaged) conversion of the two batches. As is evident the reported average conversion from the batch reaction (80%) is within 1% of the readings generated from the viscometer and the Viscosity Conversion Chart (80.78%). This indicates the viscosity chart is an adequate method for measuring conversion in this project.

4.6.3 Reaction-Time Dependant Conversion

In order to establish the limits and extents that were attainable within the time period of *30mins* for the pre-reactor, an experiment was set-up. Three stoichiometric batch reactions were set up next to each other. Each batch experiment had identical magnetic stirrers and vessels. Three separate methanol and KOH mixtures were produced consisting of 126*ml* of methanol and 7*g* of KOH and then all mixed together. The required amount of 126*ml* of methoxide was placed into the respective vessels. The stirrers were turned on and once 1*l* of sunflower oil was added to each vessel the time recorded.

The experiment was conducted at room temperature as to mimic the pre-reactor on the rig. Samples were taken at 10 minute intervals. Therefore vessel A was sampled at 18, 28 and 38 minutes; vessel B was sampled at 19, 29 and 39 minutes; vessel C was sampled at 20, 30 and

40 minutes. Using Equation 5 and Equation 6 the conversions for each of the samples was calculated (Appendix B.6). The below graph illustrates the conversion

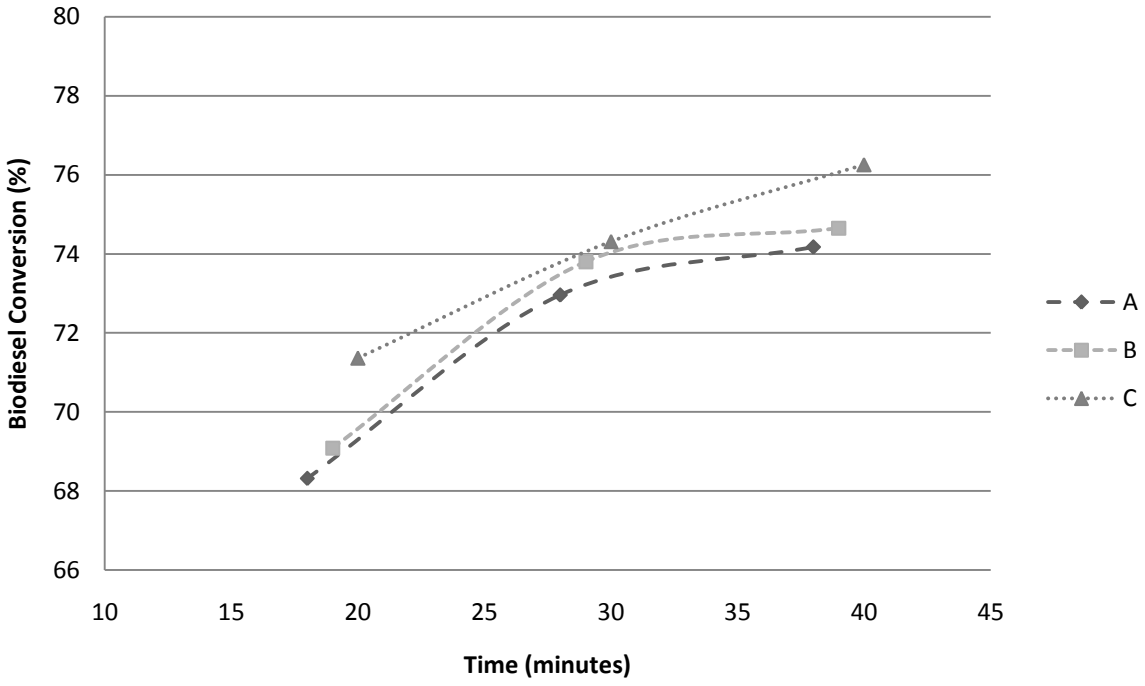

Figure 4-3 Conversion versus Residence Time for Batch Reactions

It is evident that from 30 minutes of residence time, conversion of the biodiesel should be in the range of approximately 72-74%. This conversion could be a potential target to expect from the pre-reactor in the rig; however continuous processes do vary from batch process.

4.7 Modelling of Vapour-Liquid Equilibrium in the Reboiler

In order to obtain a rough estimate of what occurred in the vapour liquid equilibrium that was generated in the unit during the experimental runs Raoult's Law was used. The equations in Chapter 2.8 (Equation 1 and Equation 2) were used in a computer program (Appendix B.7) in order to solve for the respective vapour mole fractions. The mixtures in this project were assumed ideal so the calculations can be performed. As the unit operated at atmospheric pressure, it is fair to assume that the vapour would follow the ideal gas laws. This would need to be further established in subsequent work. Three scenarios for molar ratios were computer modeled using the data generated from the mass balance. The data from the mass balance was taken from Stream 2, and Stream 3 (Chapter 3.4.4). Two sets of data were taken, namely 50%

conversion from the pre-reactor and 60% conversion from the pre-reactor. The modeled scenarios were each run at 50% and 60% conversion from the pre-reactor

- Scenario 1 was based on: Stream 2; 3:1 methanol to oil feed ratio and computing the vapour compositions for 92^{o}C, 110^{o}C and 140^{o}C.
- Scenario 2 was based on: Stream 2; 4:1 methanol to oil feed ratio and computing the vapour compositions for 92^{o}C, 110^{o}C and 140^{o}C.
- Scenario 3 was based on: Stream 3; 20:1 methanol to oil feed ratio and computing the vapour compositions for 90^{o}C, 110^{o}C and 140^{o}C.

Scenario 1 and 2 were run at 92^{o}C. At 90^{o}C there were concerns with vapour composition consistency. The computer modeling was performed after the experimental runs. The results from the model are reported in Chapter 5.5.

4.8 Conclusion

In this chapter the batch and experimental test trials were described, as was the method used for sampling and analysis of samples. The results from the experimental trials are described in the following Chapter 5. The results of the batch experiments combined with the vapour liquid equilibrium scenarios in this chapter were intended for giving guidelines of what could be expected from the test unit in terms of feasibility of biodiesel production. The biodiesel conversion chart allowed for samples to be taken from the test rig to be used in clarifying the potential of the unit to produce biodiesel.

5 Results

5.1 Introduction

This chapter focuses on reporting the results derived from both the commissioning tests and the experimental runs. The commissioning runs consisted of 6 runs. The experimental runs were divided into reboiler temperature runs (10 runs) and catalyst surface area and primer mix runs (4 runs). The commissioning runs were aimed at understanding the behaviour of the test rig and the experimental runs which followed the commissioning runs were performed to identify the best results from the test rig. This chapter incorporates the commissioning and experimental run results and analyses of the samples taken as well as a brief description of each run. Included also is an overall test rig mass balance as well as the vapour liquid equilibrium results.

The commissioning runs were performed so as to understand the functionality, behaviour, operability of the equipment and ability to reproduce results. These runs were terminated once sufficient conversion of the vegetable oil to biodiesel was achieved. The experimental runs were carried out to establish, once again, the operability of the unit and in doing so test whether or not the novel configuration was a feasible option in producing biodiesel. The data obtained from all the runs are reported below.

5.2 Results from Commissioning Runs

The commissioning runs focused on the test rig's ability to reproduce results and included modifications and adaptations to the test rig and experimental procedure. The set temperature for the runs at the reboiler was 70^{o}C, except for Run 6 in which the temperature was ramped to 90^{o}C. The data from the commissioning runs can be found in Appendix C and explained below.

Run 1. This run followed the standard experimental method. From Run 1, proof was found that the high viscosity of the liquid within the reactor would directly affect the test rig throughput and the liquid level in the pre-reactor. From this it was deduced that some of the

sand packing would need to be removed in order to allow for a greater flow through the column.

Run 2. As well as removing some of the sand packing (removal of 90*mm* of packing height), more methanol was added in the primer mix to allow for the formation of a lower viscosity, and therefore a higher liquid flowrate, through the pre-reactor. The reduced pre-reactor level of 79.5*mm* (average) proved to be slightly more manageable. However it did fluctuate and remained well below specification. The effect of the low liquid level in the pre-reactor meant that there was insufficient residence time and therefore a low biodiesel conversion was recorded. The amount of catalyst (KOH) was decreased to 5*g/l* of oil, as no benefit was gained from a high catalyst concentration (7*g/l*) as the sunflower oil was unused and therefore low in FFA. Conversion was seen to improve slightly relative to Run 1 but this can be attributed to the excess methanol added in the primer mix.

An additional problem that occurred in both Run 1 and Run 2 was a "blow-out". In a blow-out the rig would force all the liquid out of the re-boiler via the hydraulic leg. This is caused by vapour pressure increase above the reboiler due to reboiler heating. The pressure increase was a result of the large amount of methanol vapourisation. A "blow-out" can also cause the thermocouple to misread the temperature in the reboiler which in turn could cause the reboiler to overheat. This is addressed in the subsequent runs.

Run 3. The methanol in the primer mix was returned to its original concentration. The amount of catalyst was returned to the original value of 7g/l of oil. A litre of Biodiesel was added to the primer mix. Biodiesel is a co-solvent to the methanol and the sunflower oil. The advantage of adding the biodiesel to the pre-reactor is to reduce the viscosity of the liquid in the pre-reactor without the addition of excess methanol; it also helps in overcoming mass transfer issues and hence aids the forward reaction.

An overhead stirrer was also attached to the rig to assist in mass transfer restriction that occurs in the initial phases of the reaction. The level in the pre-reactor fluctuated and was still below specification. Varying the speed of the mixer did not cause any drastic effects on the pre-reactor liquid level height, the viscosity of the liquid or the conversion.

To rectify the issues with "blow outs", the glass pressure relief U-tube was removed and replaced with tubing that consisted of a smaller height U-tube (therefore reducing the pressure head). By placing a smaller liquid head in the relief system, the rig was allowed to reach steady state without a blow-out occurring, because the smaller head allowed for some flexibility i.e. the liquid in the relief tube would move rather vigorously before steady state was reached. Too much liquid in the relief system would result in a greater pressure head and therefore cause the biodiesel to come out of the relief system and cause a blow-out. Attached to the U-tube was an outlet that led to a separate beaker to collect any liquid. In the event of a sudden "blow out" the U tube would relieve any excess pressure and therefore ensure that the liquid was not flushed out of the reboiler.

During this Run 3, the overall conversion was greatly improved.

Run 4. In order to keep the liquid level in the pre-reactor high and increase the residence time in the pre-reactor, 1*l* of biodiesel instead of 2*l*, was added to the packing prior to the run. The decrease in biodiesel in the primer, and hence the amount of biodiesel in the packing, would cause a more viscous mixture, during the run, hence slowing flow and as a result increasing residence time. It was decided not to alter the pump flowrates as they were not easily calibrated and often calibrated settings would not produce the required flowrates. The liquid level in the reboiler was still found to fluctuate.

Biodiesel conversion in Run 4, in comparison to Run 3 had decreased to the levels obtained in Run 2.

Run 5. In this run, conditions were kept similar to those of Run 4, however the dump valve located at the bottom of the test rig was kept slightly open, in order to drain any glycerol. The quantity of biodiesel added to the packing was increased again to 2*l*. It was found that glycerol would form in the lower section of the reboiler. Being more viscous than biodiesel, would cause blockages in the hydraulic leg (exit pipe), and cause the level in the reboiler to rise.

Small amounts of methanol were found to exit from the modified U tube (relief system) which caused concern with regard to the overall conversion of the sunflower oil, as the

methanol escaped the process. A decision was made to add a condenser to collect the methanol vapour. In spite the escape of methanol vapour from the pressure relief system, the column still maintained greater than atmospheric pressure (marginally).

The level in the pre-reactor was found to be stable and conversion results improved and became consistent.

Run 6. The results achieved in Run 5 meant only small modifications were needed to be made in Run 6. The 2*l* of biodiesel in the packing was returned to 1*l* to ensure minimal impact on the results. In response to this, the feed pumps were controlled manually in order to keep the pre-reactor level between 200*mm* and 300*mm*.

The temperature in the reboiler was ramped up to 90^{o}C during this run to see the effect this would have on the overall conversion. A problem however occurred with the methanol feed line and insufficient methanol was pumped through the reactor. This resulted in a low overall conversion of sunflower oil. However, conversion results for the duration of the run were consistent.

A general trend was found to occur in all the commissioning runs. The pre-reactor level would begin low and, dependent on the extent of conversion, would remain low or gradually increase to the point where the feed pumps would have to be shut down. Maintaining a consistent liquid level in the pre-reactor proved to be challenging but vital in obtaining consistent results. The commissioning runs allowed for an improved rigorous start-up procedure in order to achieve consistent results.

5.3 Results from Experimental Runs: Temperature Runs and Alternate Packing

In keeping with the general experimental procedure, the run time of the experimental runs was kept at three hours and samples were taken every 20*mins*. The experimental runs focused on the oil conversion and the residence time at different temperatures, different column packing and molar feed ratios.

5.3.1 Calculations and Assumptions

The results from the experimental runs were considered as follows:

i) All samples were taken once test rig was considered at steady state;

ii) A time shift comparison of results was made comparing samples taken during steady state, for example: a sample taken from the pre-reactor after 20*mins* into the run was compared with a sample from the reboiler after 40*mins* into the run.

The steady state graphs presented below are therefore represented with respect to reboiler elapsed time. The pre-reactor results displayed on the graphs therefore refer to the given reboiler elapsed time, minus 20 minutes. The overall average conversions were calculated from samples taken when the process was at steady state.

The results giving the percentage increase in conversion were calculated by comparing the samples taken from the pre-reactor and the samples taken from the reboiler. These values were also subjected to a time shift. Average conversion values for the period when the system was at steady state were used in the following equation. Average values were used to remove variances that may have occurred.

$$\boldsymbol{Percent\ Increase} = \frac{\boldsymbol{ARC}(\boldsymbol{i} + \boldsymbol{20mins}) - \boldsymbol{APC}(\boldsymbol{i})}{\boldsymbol{ARC}(\boldsymbol{i} + \boldsymbol{20mins})} \times \mathbf{100}\%$$

Equation 8

Where *ARC* – Average Reboiler Conversion over random time interval *i* plus 20 minutes; *APC* – Average Pre-reactor Conversion at time interval *i*; *i* – Is the selected time interval when the system was at steady state.

The average conversion difference was calculated by averaging each reboiler conversion and subtracting the average of the pre-reactor conversion. These were taken from when the system was at steady state and were also subjected to a time shift. The following equation was used

$$\boldsymbol{Average\ Difference} = \boldsymbol{ARC}(\boldsymbol{i} + \boldsymbol{20mins}) - \boldsymbol{APC}(\boldsymbol{i})$$

Equation 9

The residence time in the pre-reactor was calculated only over the period of time when the process was at steady state. The residence time was calculated from the liquid level height in the pre-reactor using the known heights from the rig and the run specific flowrates. The calculations are shown in Appendix D.1.

The flowrates and molar ratio were calculated from the amount of oil and methanol used during the 3 hour run. Measurements were taken before and after each run to determine the volume that had been pumped through the system. Multiplying the amount of sunflower oil and methanol by their densities and molecular weights, respectively, yielded the molar ratio of sunflower oil to methanol (Appendix D.2).

5.3.2 Run T1: 90^{o}C, 4.5:1

On the basis of the commissioning runs, which were run at a reboiler temperature of 70^{o}C, it was decided to increase the reboiler temperature in the experimental runs to 90^{o}C, in order to improve conversion. It was thought that an increase in temperature in the reboiler would cause more methanol to evaporate and become available for reaction with the sunflower oil once it condensed on the packing. The molar feed ratio of the methanol to oil was found to be 4.5:1. This meant the reboiler was operating above stoichiometric ratio and would drive the forward reaction hence producing a higher mass of biodiesel. The graph below (Figure 5-1) illustrates the achieved conversion with time for the duration of the run.

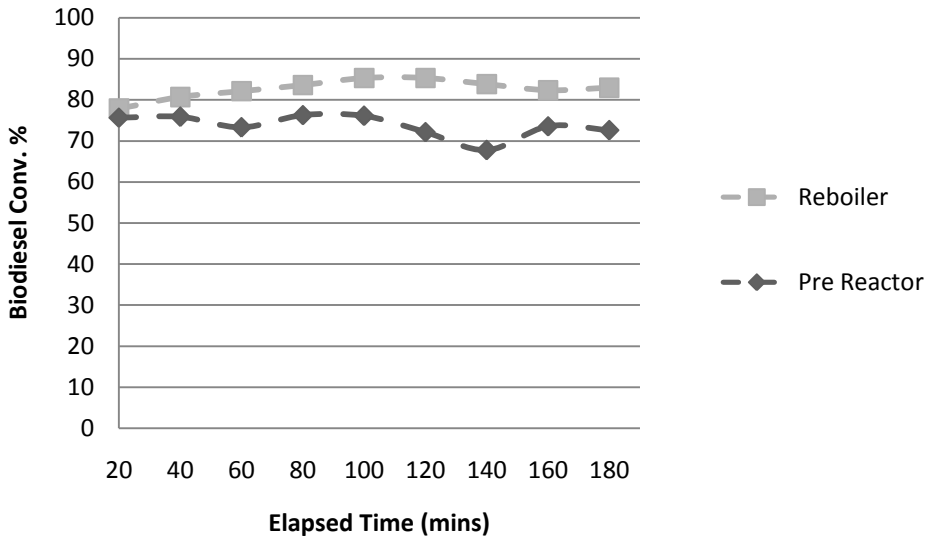

Figure 5-1 Run T1: 90°C, 4.5:1

As can be seen from the above figure the reboiler provided a relatively consistent conversion for the duration of the run.

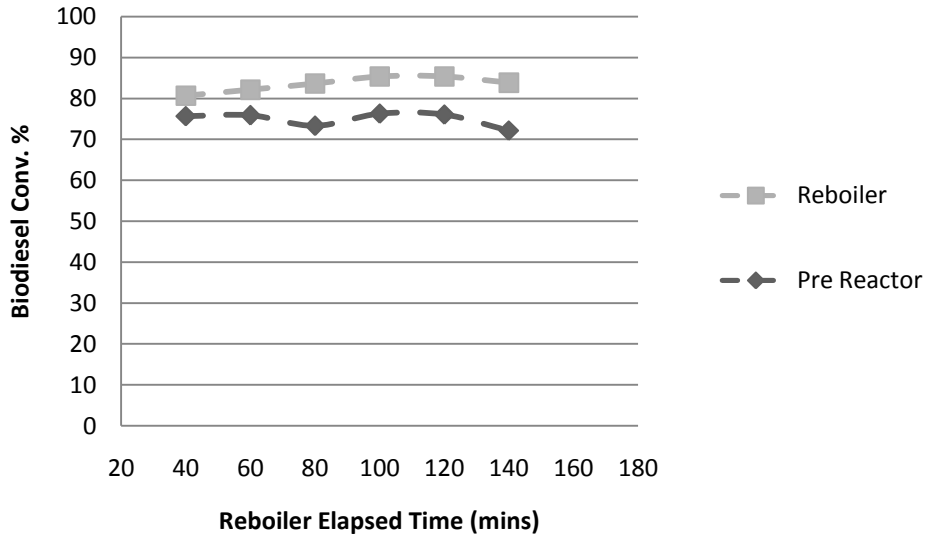

Figure 5-2 T1: 90°C, 4.5:1 at Steady State

The system was at steady state from 20 minutes through to 120 minutes (Figure 5-2), after this period conversion was not consistent. The average recorded flowrate from the run was 4*l/hr* which produced a pre-reactor residence time of 29 minutes during the steady state period; the average overall conversion was 82%. The percent increase in conversion from the pre-reactor was 9%.

5.3.3 Run T2: 90°C, 3.8:1

This run was performed at 90°C. The molar feed ratio was determined to be 3.8:1. The following graph illustrates the findings (Figure 5-3).

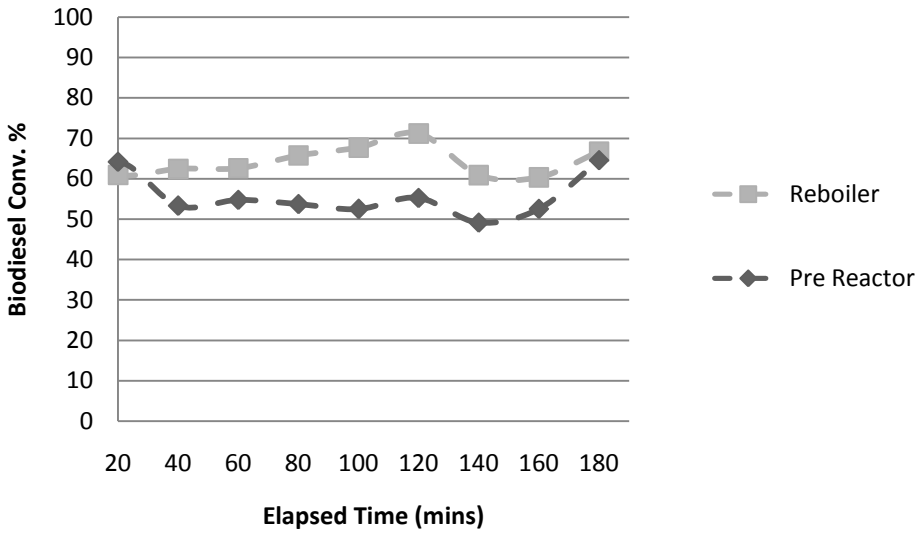

Figure 5-3 Run T2: 90°C, 3.8:1

After 40 minutes the rig showed some consistency however after 120 minutes the behaviour of the rig changed. The initial variances can be attributed to operator controlled feed supply.

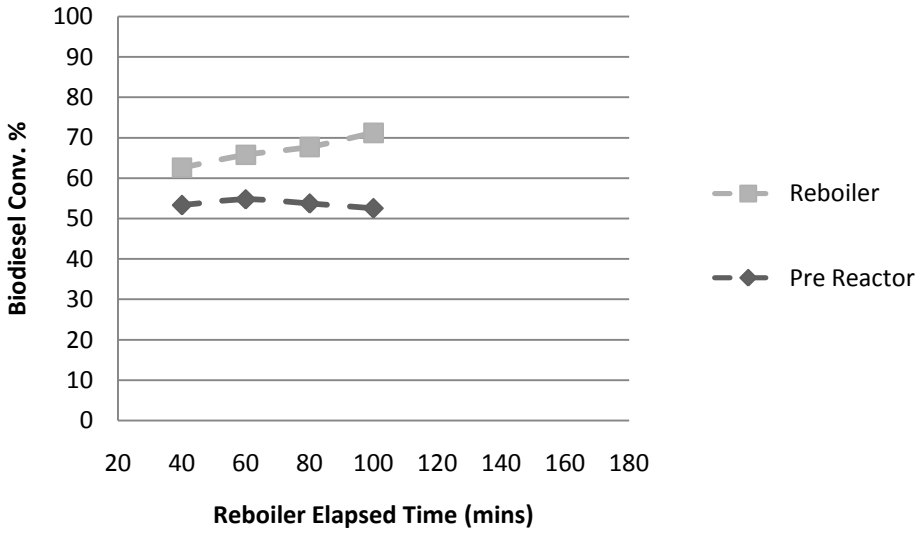

Figure 5-4 Run T2: 90°C, 3.8:1 at Steady State

The average conversion at steady state was 67% (Figure 5-4). The recorded flowrate was 3.9*l/hr* with a pre-reactor residence time of 36 minutes over the steady state period. The average percent increase in conversion was 20%.

5.3.4 Run T3: 90°C, 4.0:1

This run was kept the same as in Run T2, although the feed pumps were altered slightly. The temperature remained at 90°C and the methanol to oil feed ratio was observed to be 4.0:1. The following results were obtained (Figure 5-5).

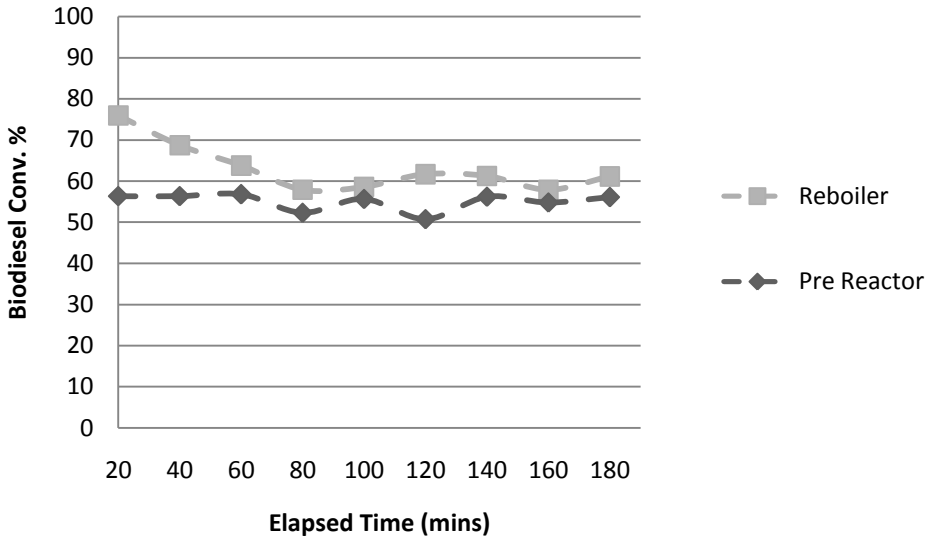

Figure 5-5 Run T3: 90°C, 4.0:1

The results for the majority of the run were erratic and this can be attributed to feed supply inconsistencies. The initial high reboiler conversions can be attributed to the primer mix in the rig. The rig seemed to operate at steady state for a short period of time.

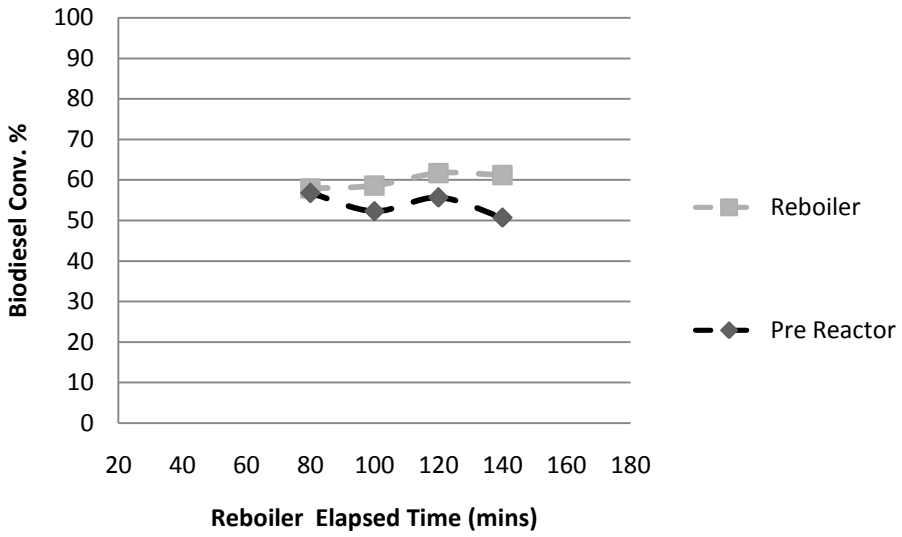

Figure 5-6 Run T3: 90°c, 4.0:1 at Steady State

The average reboiler conversion achieved was 60% at steady state (Figure 5-6). The recorded flowrate for the run at the steady state was 4.7*l/hr*. This gave a pre-reactor residence time of 30 minutes. The average increase in conversion was 10%. The average conversion is lower than the conversion achieved in Run T2 even though Run T2 had a lower methanol to oil ratio but a higher residence time.

5.3.5 Run T4: 110°C, 3.0:1

Run T4 was performed at 110°C with a methanol to oil feed ratio of 3.0:1. The graph below (Figure 5-7) illustrates the conversions achieved.

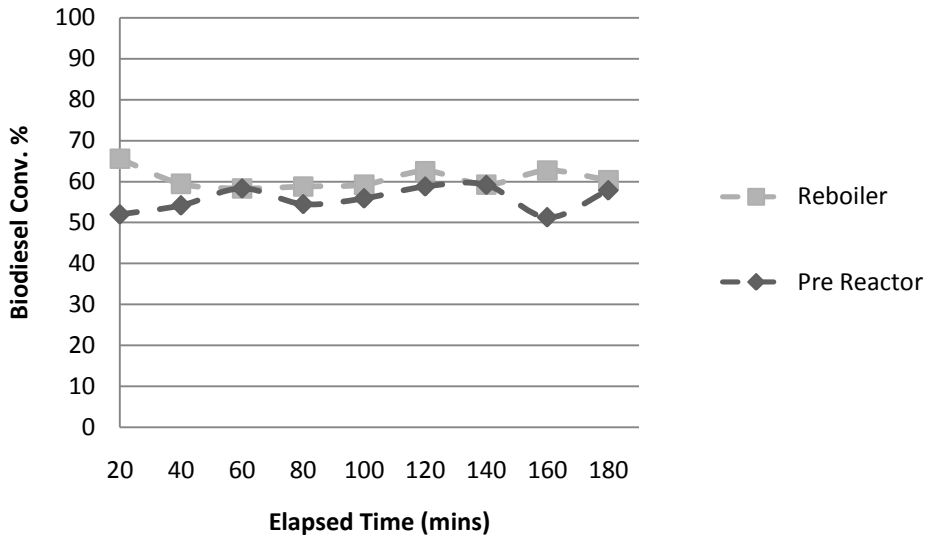

Figure 5-7 Run T4: 110°C, 3.0:1

As can be seen above the reboiler seemed to operate consistently over a large portion of the run. The high initial conversion can be once again attributed to the biodiesel primer in the column.

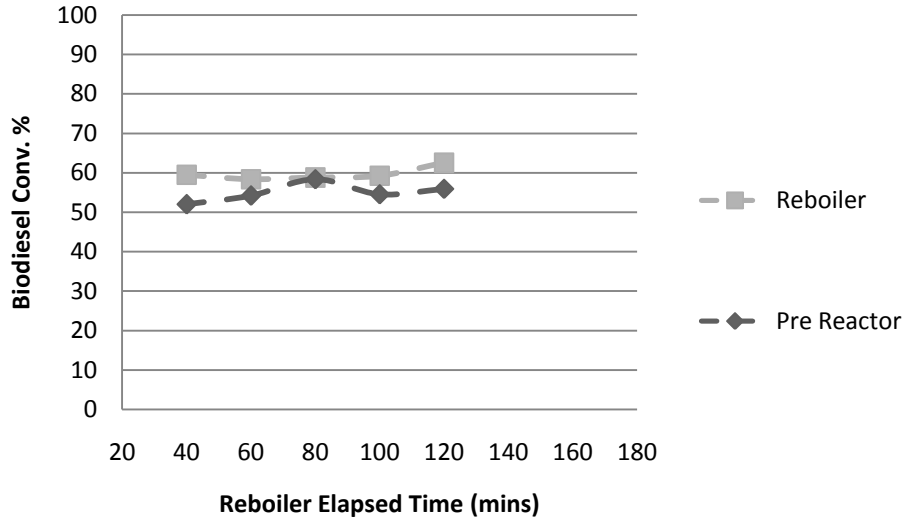

Figure 5-8 Run T4: 110°C, 3.0:1 at Steady State

The steady state calculations yielded a conversion of 60% from a flowrate of 4.5*l/hr* and a pre-reactor residence time of 28 minutes. The average percent increase in conversion from the pre-reactor to the reboiler was 8%. The spike in pre-reactor conversion can be related to the fluctuations in the pre-reactor liquid level (Figure 5-8).

5.3.6 Run T5: 140°C, 3.1:1

This run was performed at 140°C with a methanol to oil feed ratio of 3.1:1. The below graph (Figure 5-9) illustrates the conversion with time from the run.

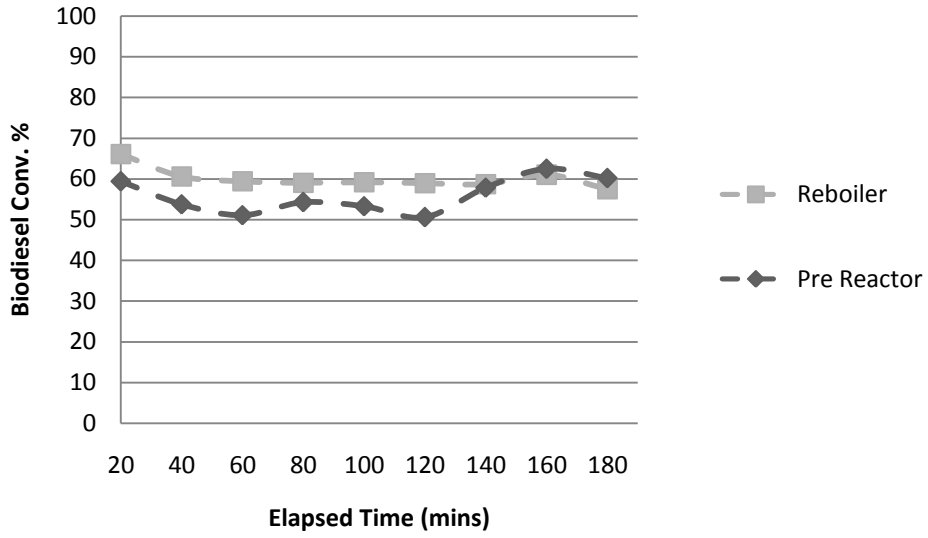

Figure 5-9 Run T5: 140°C, 3.1:1

Reboiler conversion remained fairly consistent for the duration of the run. The pre-reactor conversion was seen to increase to levels above the reboiler conversion. From the experiment it was also noted that methanol was being discharged from the safety valve into the condenser (approx. 3*ml*). This would mean that less methanol was available to condense and come into contact with the unreacted sunflower oil.

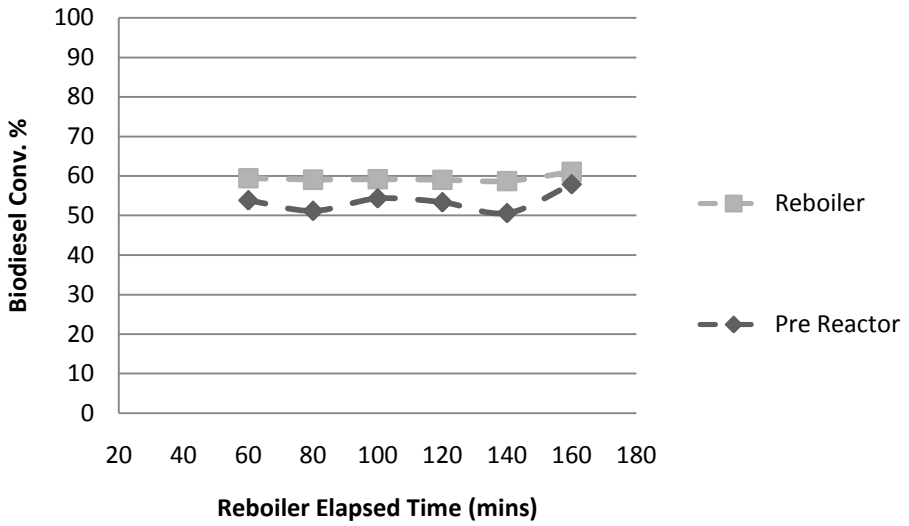

Figure 5-10 Run T5: 140°C, 3.1:1 at Steady State

At steady state, the rig obtained an average conversion of 59%, (Figure 5-10). The flowrate was 4.5*l/hr* with a pre-reactor residence of time of 28 minutes over the steady state period. The average percent increase in conversion was 10%.

5.3.7 Run T6: 110°C, 3.1:1

The temperature was returned to 110°C and the methanol to oil feed ratio was observed at 3.1:1. The below graph was generated from the run.

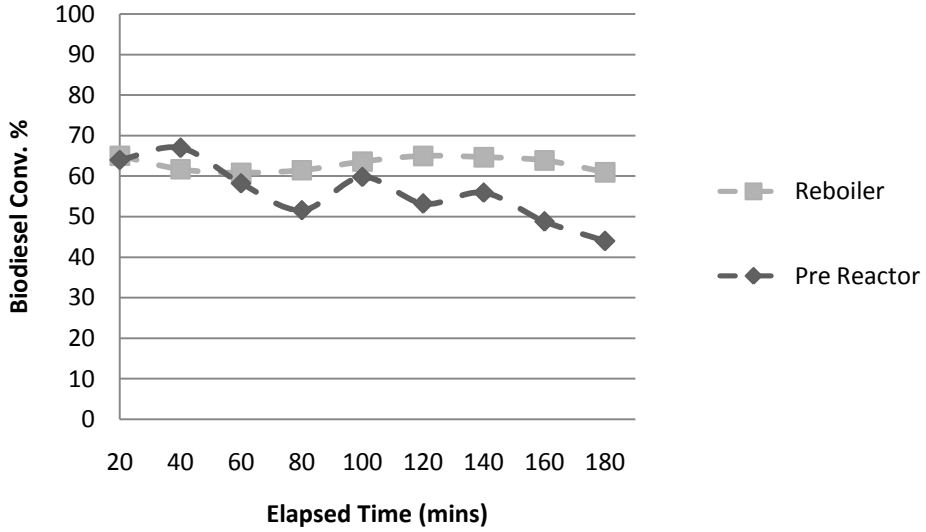

Figure 5-11 Run T6: 110°C, 3.1:1

The reboiler conversion was seen to remain consistent throughout the run. One reading however was lower than that of the pre-reactor (Figure 5-11). This reading can safely be assumed to have been taken before steady state and hence ignored.

Figure 5-12 illustrates the rig at steady state. The average conversion was 63%. The flowrate was recorded at 3.7*l/hr* with a residence time of 37 minutes in the pre-reactor during the steady state period. The average percent increase in conversion from the pre-reactor to the reboiler was 14%.

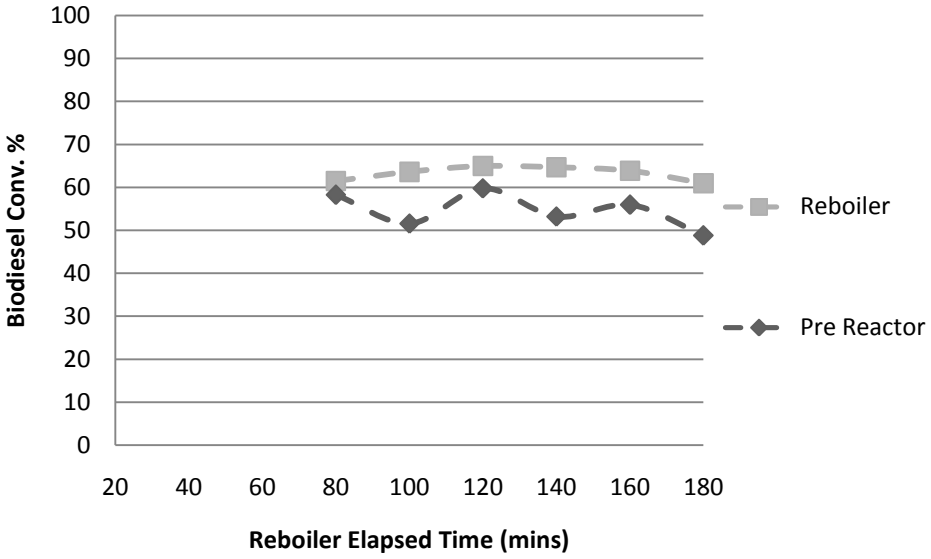

Figure 5-12 Run T6: 110°C, 3.1:1 at Steady State

5.3.8 Run T7: 70°C, 3.0:1

The temperature was decreased further to 70°C. The methanol to oil feed ratio was observed at 3.0:1.

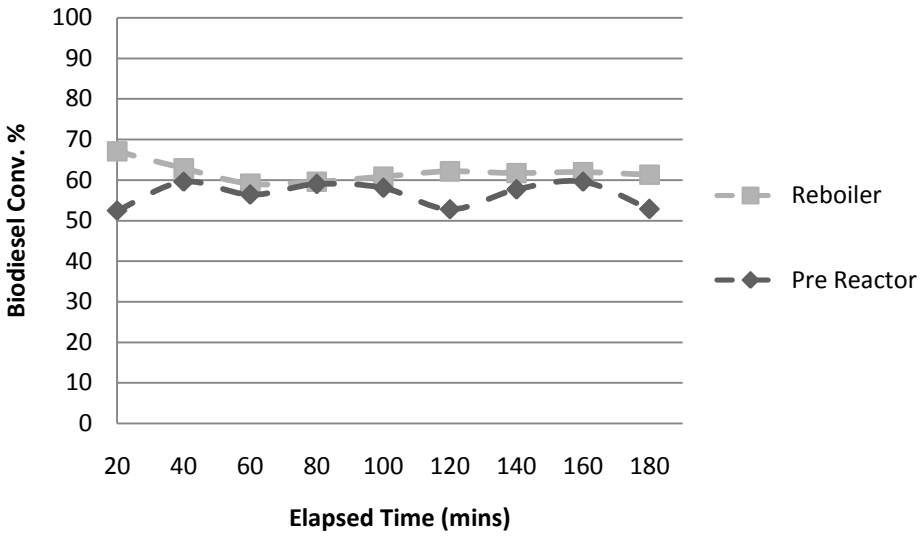

Figure 5-13 Run T7:70°C, 3.0.1

The above graph (Figure 5-13) illustrates the conversion achieved as a function of time. It is evident the reboiler offers only a slight improvement in conversion.

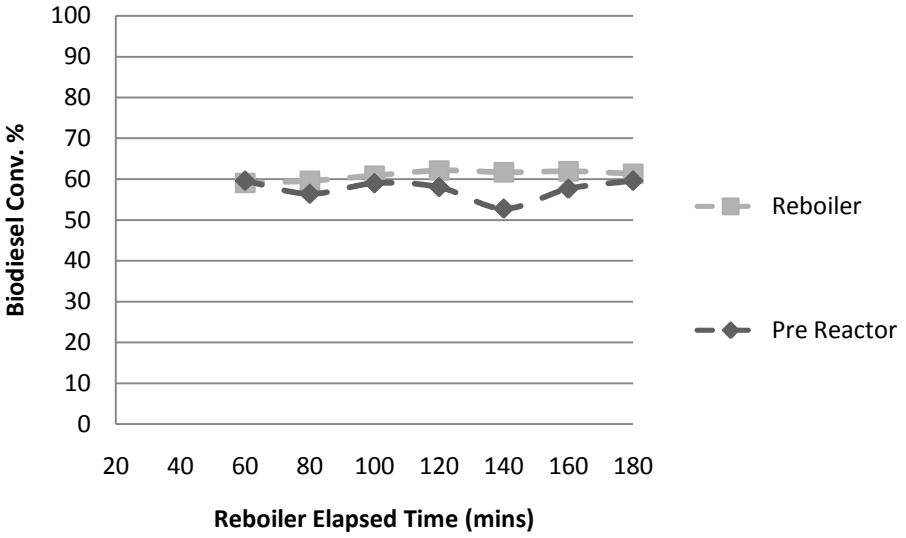

Figure 5-14 Run T7:70°C, 3.0.1 at Steady State

At steady state the average overall conversion was 61%. The flowrate was 3.2*l/hr* which produced a 40 minute residence time in the pre-reactor during the steady state analysis. The average percentage conversion increase was 6%. From Figure 5-14 there is a dip in the pre-reactor conversion at 140*mins.* A point of note was that the reboiler maintained steady conversion despite a dip in conversion experienced at 140*mins* in the pre-reactor.

5.3.9 Run T8: 70°C, 3.1:1

This was a repeat of Run T7 but with an observed methanol to oil feed ratio of 3.1:1.

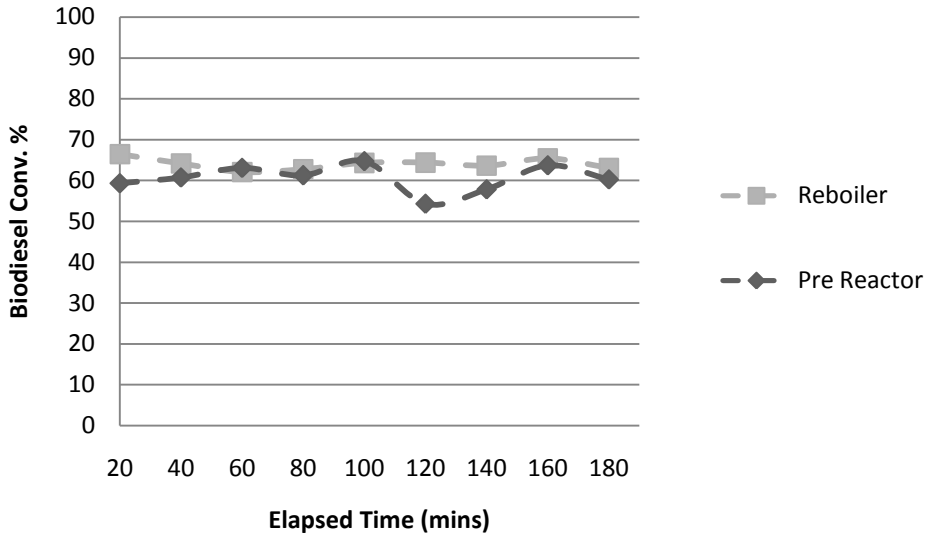

Figure 5-15 Run T8: 70°C, 3.1:1

Once again reboiler conversion remained consistent. There was a dip in conversion in the pre-reactor. At one point pre-reactor conversion seemed to be higher than conversion in the reboiler. The entire run, except for the first set of readings which may have been affected by the primer mix, were taken as steady state. The following graph (Figure 5-16) was produced assuming steady state allowing for the time shift.

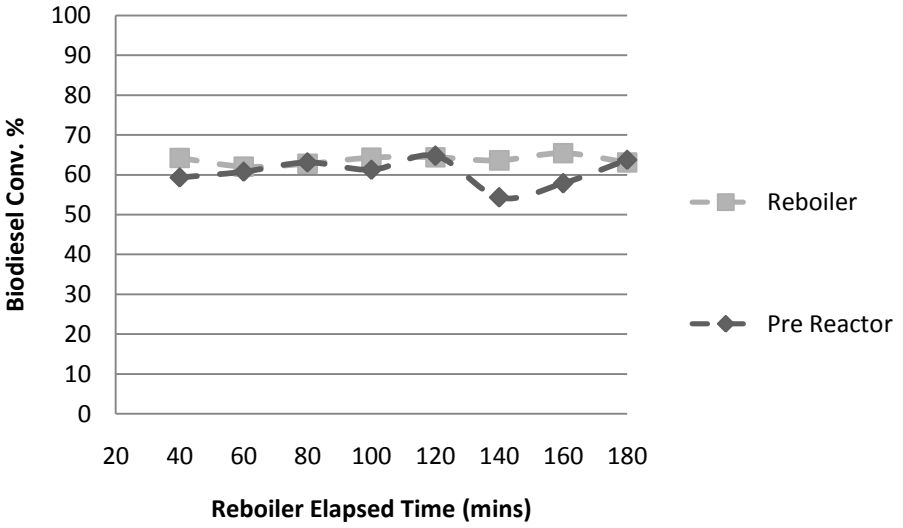

Figure 5-16 Run T8: 70°C, 3.1:1 at Steady State

This run yielded an average conversion of 64% at a flowrate of 3.2*l/hr*. The average residence time over the steady state period was 40 minutes. The average increase in conversion was 5%. This corresponds with the previous run, Run T7, which achieved an average increase in conversion of 6%.

5.3.10 Run T9: 110°C → 90°C, 3.0:1

For Run T9 it was decided to reduce the residence time in the reboiler to ensure that no reverse reaction was occurring. Initially the experiment was set to run at 110°C however it was difficult to control and a temperature of 90°C was programmed into the temperature controller (Figure 5-17). This was done after 55 minutes into the run. At high temperatures with no liquid in the reboiler the system would undoubtedly overheat. In addition to this the hydraulic leg was bypassed as the bottom valve was left open enough to ensure a liquid level height to cover the thermocouple. The methanol to oil feed ratio was constant at 3.0:1.

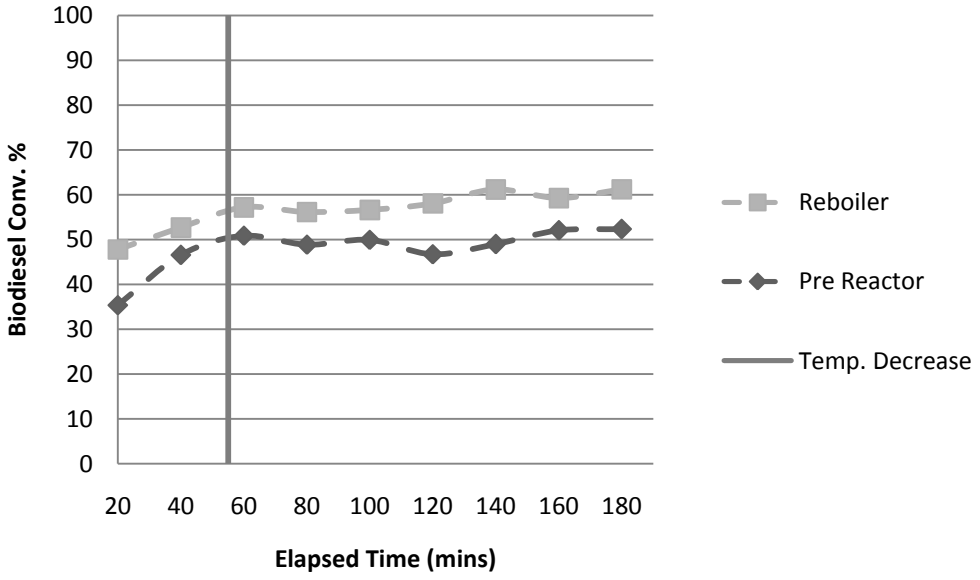

Figure 5-17 Run T9: 110°C → 90°C, 3.0:1

The liquid level height in pre-reactor (prior to the decrease in temperature and the limited flow through the bottom valve) averaged 130*mm*, which computed to a residence time of 17minutes. Furthermore, prior to limiting flow through the bottom valve, there was no residence time in the reboiler, which caused the reboiler to overheat and trip. This could explain the low initial conversions.

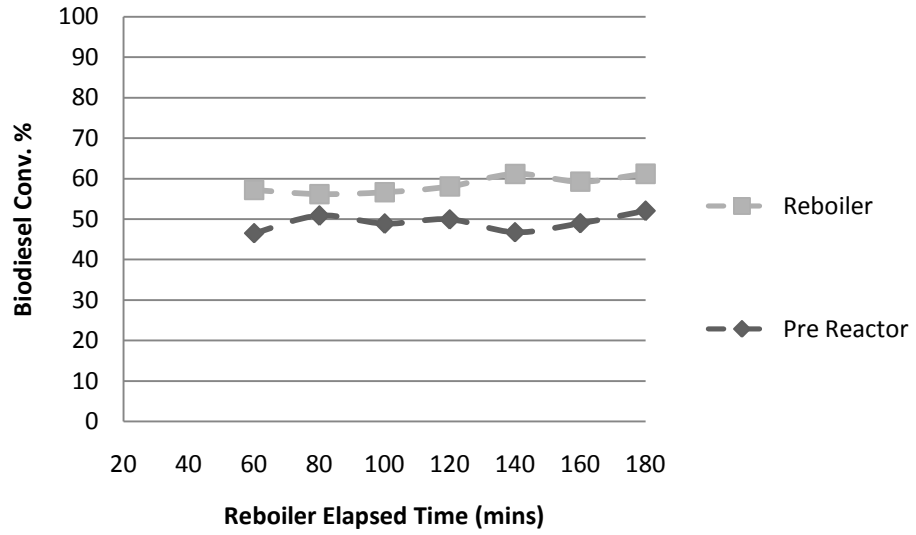

Figure 5-18 Run T9: 110°C → 90°C, 3.0:1 at Steady State

The average conversion obtained was 59%. The flowrate through the reactor was 4.5*l/hr* with a residence time of 25 minutes for the steady state range (Figure 5-18). The average increase in conversion was 9%.

5.3.11 Run T10: 25°C→30°C→40°C→50°C, 3.0:1

In order to further minimise the residence time in the reboiler but avoid the problems experienced in Run T9 (such as overheating and tripping the element), marbles, similar to those in the packing, were placed in the reboiler. The bottom valve could now be left completely open as the marbles would provide a more accurate temperature reading for the thermocouple; they would be in contact with the heating belt and the thermocouple. A slower heating program was also adopted.

Run T10 used four reboiler temperature setpoints where the temperature was allowed to increase with time using the reboiler heating belt. Reboiler temperature was changed from room temperature (25°C), to 30°C to 40°C and then to 50°C within periods of 30 minutes, 80 minutes and 130 minutes respectively. Samples were taken at 10 minute intervals. Four samples were taken at room temperature and five samples were taken for each temperature

setpoint. The methanol to oil feed ratio was 3.0:1. The following figure (Figure 5-19) represents the results from Run T10.

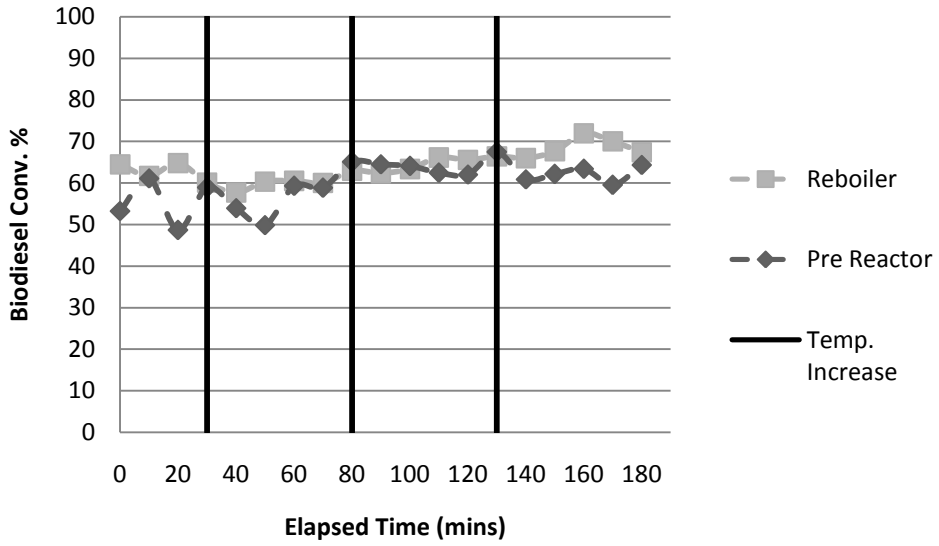

Figure 5-19 Run T10: 25°C→30°C→40°C→50°C, 3.0:1

During the run it was noted that pre-reactor liquid level did not stabilise as fast as previous runs, this would explain the fluctuations evident in Figure 5-19 from the start of the run to approximately 60*mins* into to the run. As the temperature in the reboiler increased the conversion in the pre-reactor and the reboiler also increased. The highest conversion and the most significant effect of the reboiler occurred at reboiler temperature of 50°C. The results from each reboiler temperature setting are discussed below allowing again for the time shift in the following figures respectively Figure 5-20, Figure 5-21, Figure 5-22 and Figure 5-23

Room Temperature

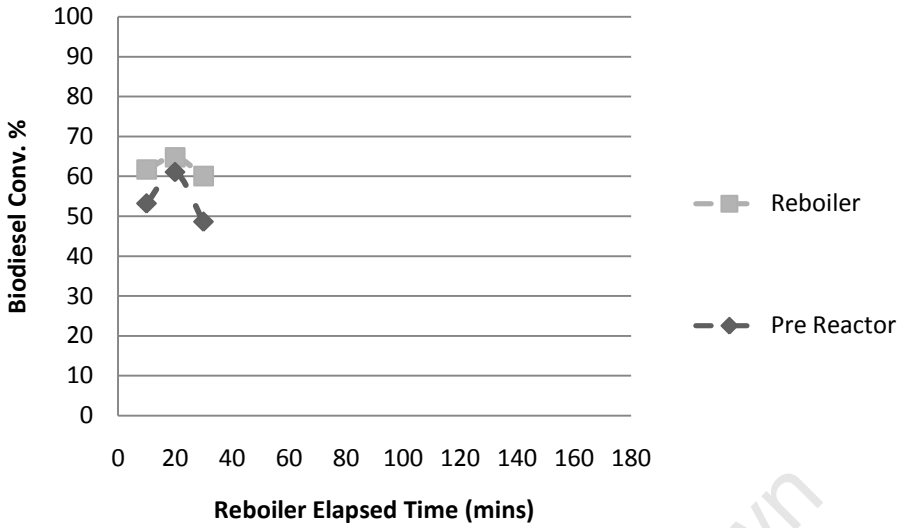

Figure 5-20 Run T10: Room Temperature, 3.0:1 at Steady State

Temperature of the reboiler set at 30^{o}C

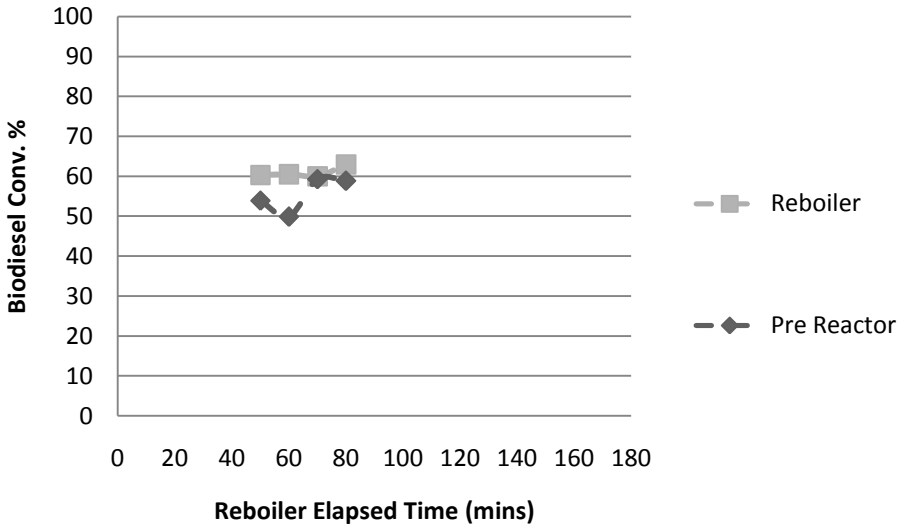

Figure 5-21 Run T10: 30^{o}C, 3.0:1 at Steady State

Temperature of the reboiler set at 40°C

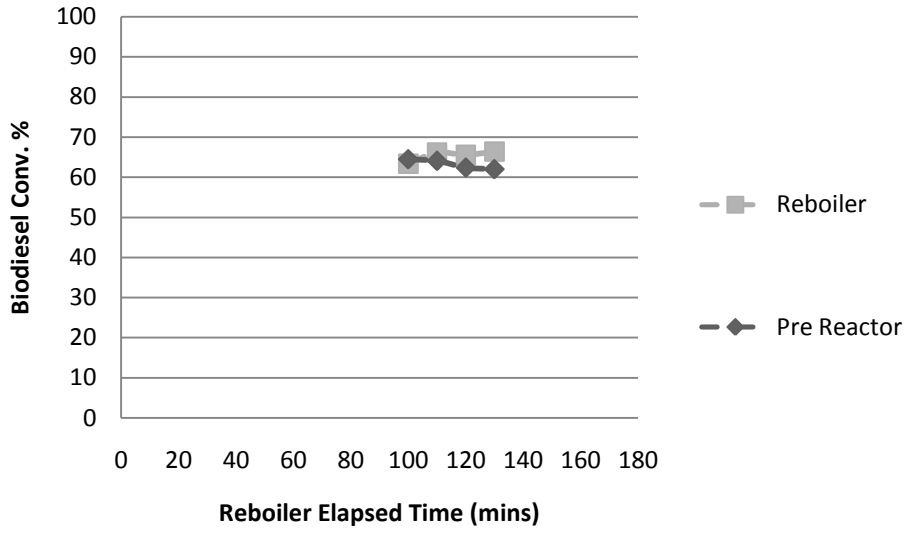

Figure 5-22 Run T10: 40°C, 3.0:1 at Steady State

Temperature of the reboiler set at 50°C

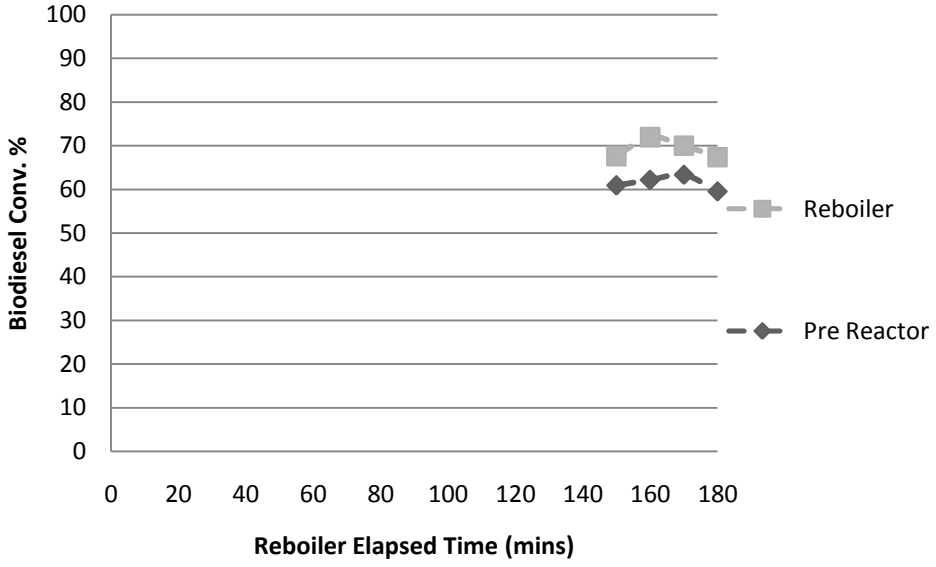

Figure 5-23 Run T10: 50°C, 3.0:1 at Steady State

Table 5-1 Run T10 Residence Times and Conversions

Reboiler Temperature	Pre-Reactor Residence Time	Conversion	Increase in Conversion
°C	Mins	%	%
Room Temp	12	62	13
30	12	61	9
40	21	65	3
50	23	69	11

The recorded flowrate for the Run T10 was 5.*3l*/hr. The above table (Table 5-1) illustrates the average conversion for different reboiler set point temperatures. The conversion in the pre-reactor was low and erratic when the rig was at room temperature. It can be assumed the process had not yet reached steady state. The reboiler contributed significantly to the overall conversion at room temperature. This confirms the positive contribution the reboiler has on conversion.

5.3.12 Run P1: 90°C, 3.0:1, Raschig Rings

Run P1 (P for packing) was carried out using ceramic Raschig rings instead of marbles. This resulted in a 23% increase in available packing surface area. The standard experimental procedure, as previously followed, remained unchanged. The marbles from the reboiler section of the test rig were also removed. The test rig bottom valve was closed sufficiently to allow the use of the hydraulic leg and draining of glycerol from the test rig. It was assumed that the greater surface area in the packing would increase the conversion by allowing for more methanol vapour to condense on more oil that covered the larger surface area. This would also increase the residence time, as flow was gravity driven and the larger surface area of marbles created a greater pressure drop. The following graph (Figure 5-24) illustrates the results obtained from this run.

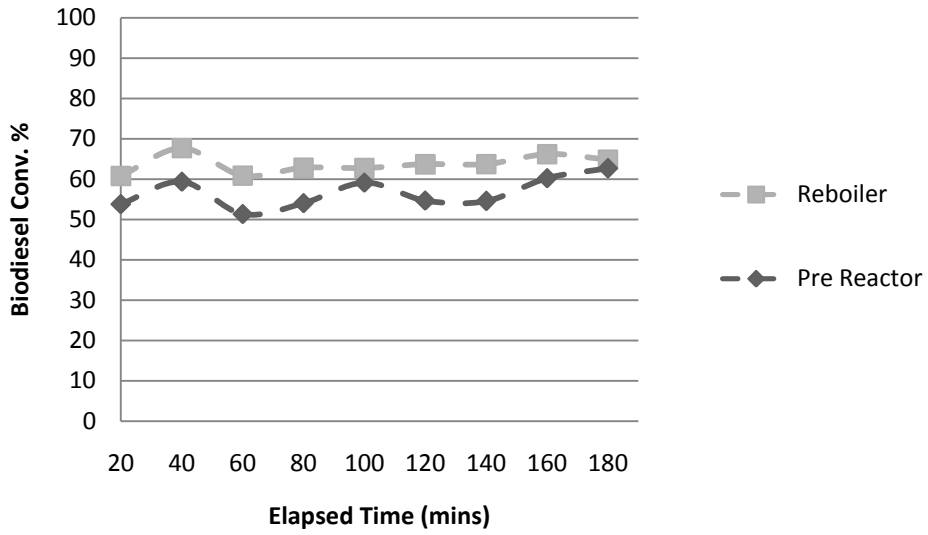

Figure 5-24 Run P1: 90°C, 3.0:1, Raschig Rings

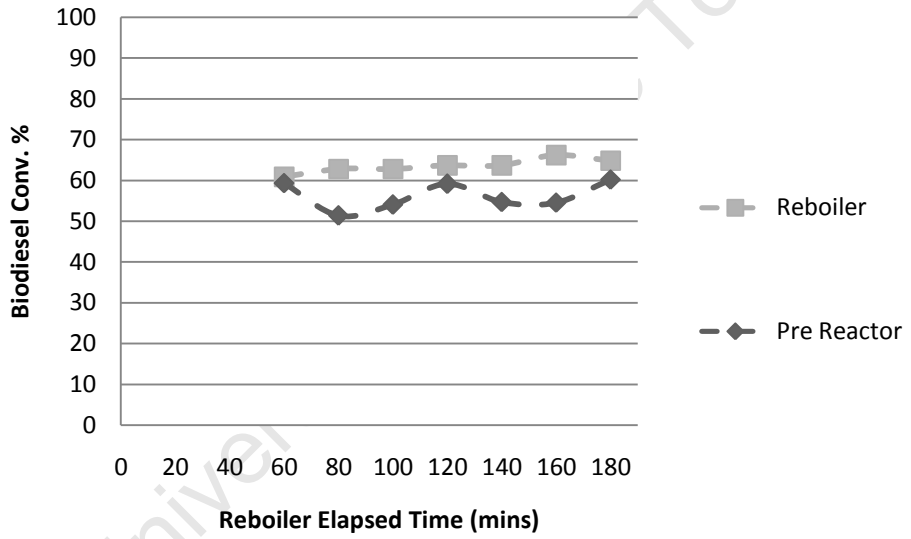

Figure 5-25 Run P1: 90°C, 3.0:1, Raschig Rings at Steady State

Figure 5-25, (above) represents the steady state analysis of Run P1. The average conversion for the steady state period was 64%. The flowrate was 4.5*l*/hr and pre-reactor residence time was found to be 22 minutes. The percent increase in conversion was 13%.The pre-reactor conversion is seen to fluctuate which can be attributed to the manual control of the feed lines. Despite these fluctuations in the pre-reactor, the reboiler conversion remained fairly constant.

5.3.13 Run P2: 90°C, 3.0:1, Raschig Rings

Run P2 was a repeat of run P1 and was performed for reproducibility. The graph below, Figure 5-26, is a representation of the runs results.

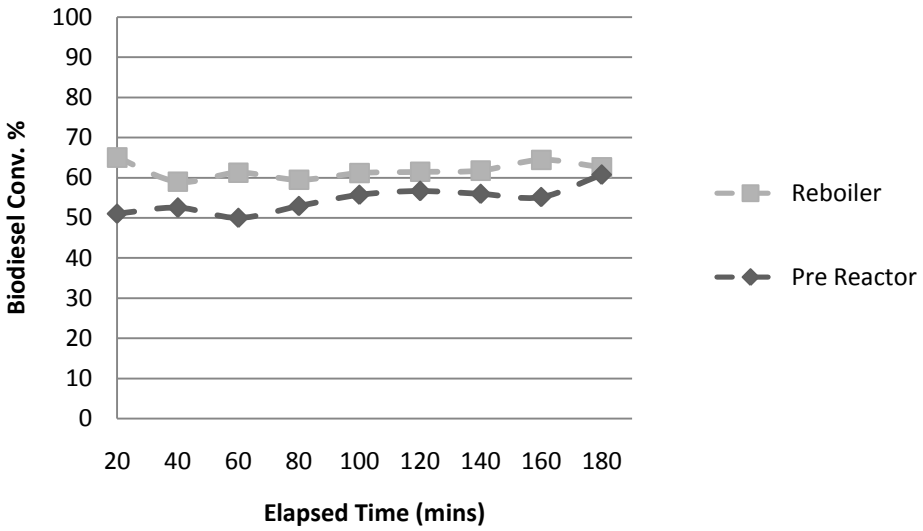

Figure 5-26 Run P2: 90°C, 3.0:1, Raschig Rings

At steady state the average conversion was 61%. A flowrate of 4.3*l/hr* produced a residence time of 23 minutes. The average increase in conversion was 13%. The average difference in conversion between Run P1 and Run P2 was 7.4% and 7.6%. There is consistency between the two runs; however the difference in their respective overall conversions can be attributed to fluctuation in the feed experienced during Run P1. From the experimental notes, 1*ml* of methanol was captured in the condenser. Figure 5-27 depicts the results at steady state, taking the time shift into account.

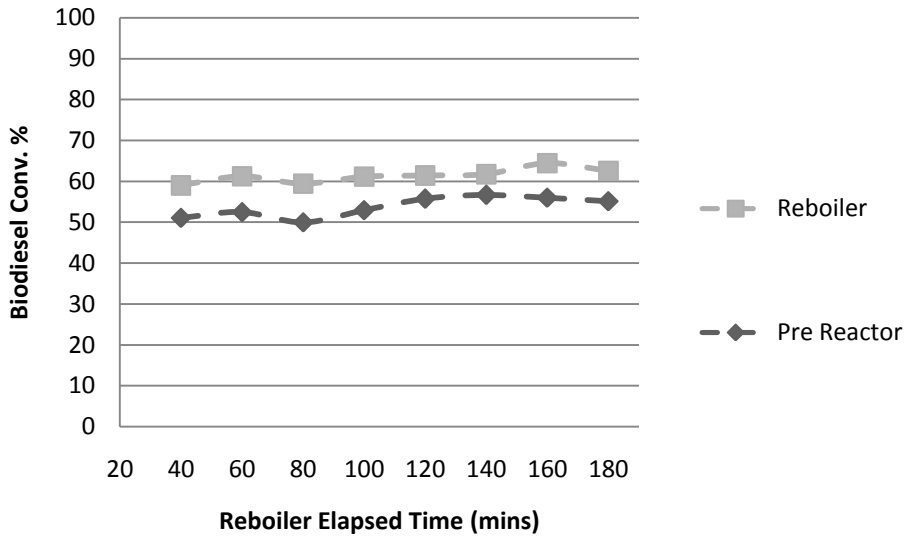

Figure 5-27 Run P2: 90°C, 3.0:1, Raschig Rings at Steady State

5.3.14 Run P3: 110°C, 3.1:1, Raschig Rings, New Primer

During this Run P3 the primer mix was changed to reduce the time lag during start-up. The primer mix was changed to 500*ml* FAME biodiesel, 1500*ml* fresh Sunflower oil and 186*ml* methanol. The temperature was also increased to 110°C. The results from this run are represented in Figure 5-28 below.

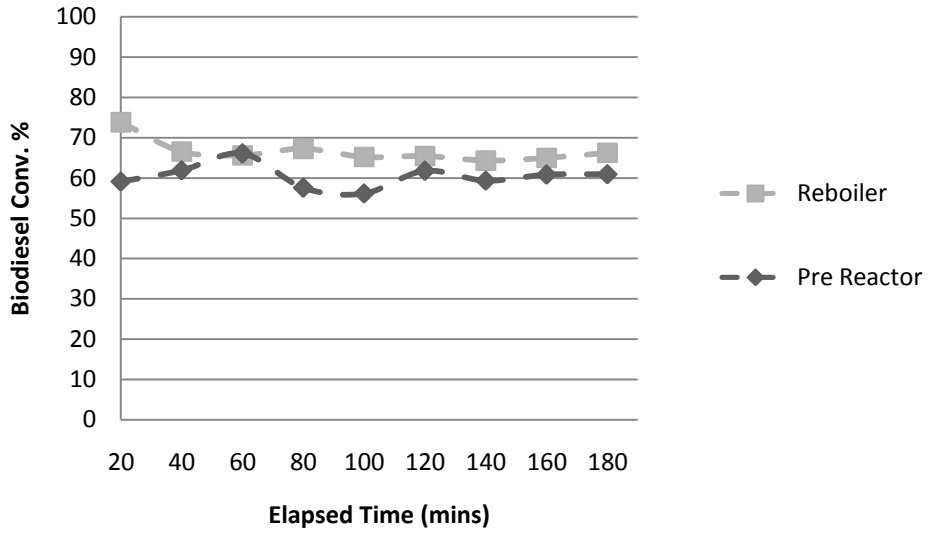

Figure 5-28 Run P3: 110°C, 3.1:1, Raschig Rings, New Primer

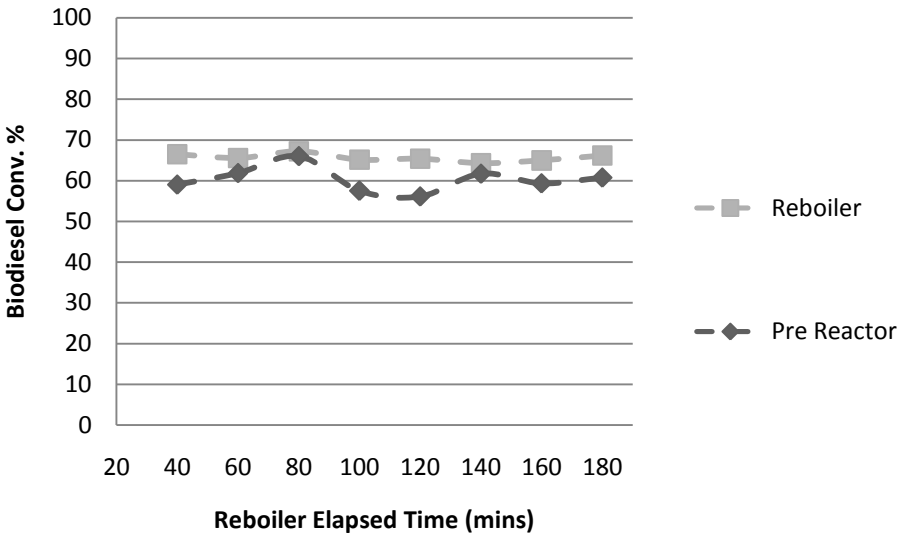

Figure 5-29 Run P3: 110°C, 3.1:1, Raschig Rings, New Primer at Steady State

The steady state calculations for Run P3 are shown in Figure 5-29. The average conversion was 66%. The flowrate was 3.4*l/hr* which meant a pre-reactor residence time of 37 minutes. The average increase in conversion over the reboiler was 8%. From the experimental notes, 2*ml* of methanol was captured by the condenser.

5.3.15 Run P4: 90°C, 3.2:1, Raschig Rings, New Primer

This was the final run performed using Raschig Rings. The temperature was returned to 90°C and the new primer mix was used.

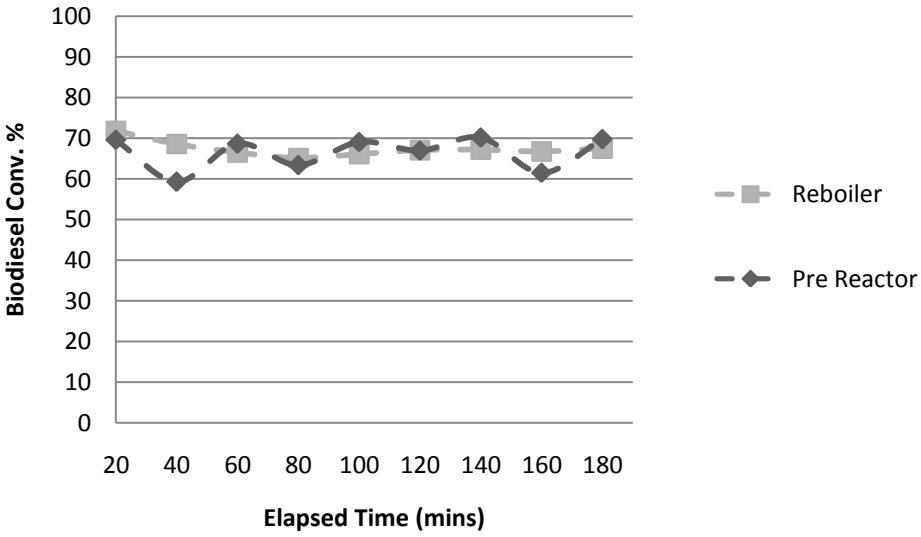

Figure 5-30 Run P4: 90°C, 3.2:1, Raschig Rings, New Primer

As can be seen from Figure 5-30 the pre-reactor conversion varied during the test run while the reboiler conversion was constant. In some instances the pre-reactor conversion was better than the reboiler conversion.

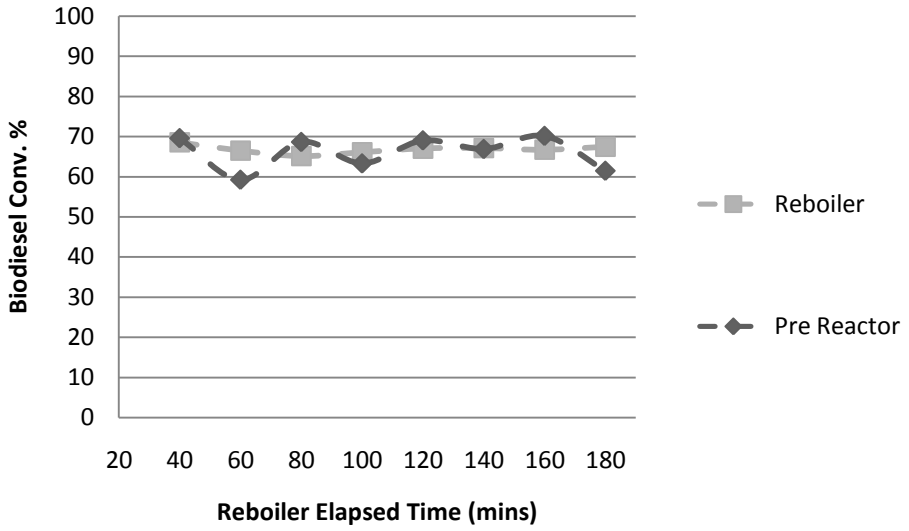

Figure 5-31 Run P4: 90°C, 3.2:1, Raschig Rings, New Primer at Steady State

At steady state the average conversion achieved was 67%. The flowrate was 3.6*l/hr* and the residence time over this period was 33 minutes. Although at times the pre-reactor conversion was higher than the reboiler conversion the average increase in conversion with time was 1.1%.

5.4 Overall Mass Balance

Three runs were selected for the overall mass balance. The purpose was to account for all the substances and to check the effectiveness of the condenser. The approach was simple. The mass of each reactant was measured before the start of the test run. When the test run was concluded the mass of all of the products together was recorded. Table 5-2 below illustrates the findings. Detailed calculations are available in the Appendix C.2

Table 5-2 Overall Mass Balance for Run P2, P3 and P4

Run	Mass In (g)	Mass Out (g)	Difference (g)
Run P2: 90^{o}C	16238	16195	-43
Run P3: 110^{o}C	12834	12772	-62
Run P4: 90^{o}C	13304	13284	-20

The reduction in the mass of the liquid products can be attributed to liquid retained in the test rig (e.g. in the sand packing). The mass loss at the higher temperature test run (110^{o}C) can be attributed to methanol evaporation because the product tank was open to the environment.

It is reasonable to assume that the amount of methanol exited the test rig via the pressure relief system was negligible. This assumption is also supported by the fact that only a small quantity of methanol reported in the condenser: 2*ml* of methanol for run P2, 2*ml* of methanol for run P3 and 1*ml* of methanol for run P4.

5.5 Vapour Liquid Equilibrium Results

Using the three scenarios established in Chapter 4.7, the following tables were generated using the computer program (Fortran) described in Appendix B.7. The feed data, which were in fact the input data for the model, were obtained from a mass balance simulation, (using the spreadsheet used in Appendix A.5, in which 50% and 60% conversion from the pre-reactor were considered.

Table 5-3 Scenario 1

Molar Ratio	3:1			**Feed Stream Conv.**	**Amount of total Methanol in liquid Product Stream from Feed Stream (%)**		
Feed Data					**92°C**	**110°C**	**140°C**
	50% Conversion	**60% Conversion**		**50%**	98.03	44.40	16.94
	mol/hr	**mol/hr**		**60%**	NAN	62.16	23.71
Biodiesel	7.80	9.36					
SFO	2.60	2.08			**Methanol composition in Liquid Product Stream (%)**		
Meth	7.80	6.24			**92°C**	**110°C**	**140°C**
Glyc	2.60	3.12		**50%**	37.04	21.04	9.23
				60%	37.04	21.04	9.23

Table 5-4 Scenario 2

Molar Ratio	4:1			**Feed Stream Conv.**	**Amount of total Methanol in liquid Product Stream from Feed Stream (%)**		
Feed Data					**92°C**	**110°C**	**140°C**
	50% Conversion	**60% Conversion**		**50%**	58.82	26.64	10.16
	mol/hr	**mol/hr**		**60%**	74.86	33.90	12.93
Biodiesel	7.80	9.36					
SFO	2.60	2.08			**Methanol composition in Liquid Product Stream (%)**		
Meth	13.00	11.44			**92°C**	**110°C**	**140°C**
Glyc	2.60	3.12		**50%**	37.04	21.04	9.23
				60%	37.04	21.04	9.23

Table 5-5 Scenario 3

Molar Ratio	20:1			**Feed Stream Conv.**	**Amount of total Methanol in liquid Product Stream from Feed Stream (%)**		
Feed Data					**90°C**	**110°C**	**140°C**
	50% Conversion	**60% Conversion**		**50%**	29.17	11.85	4.52
	mol/hr	**mol/hr**		**60%**	36.75	14.94	5.69
Biodiesel	14.82	14.98					
SFO	0.26	0.21			**Methanol composition in Liquid Product Stream (%)**		
Meth	44.99	35.99			**90°C**	**110°C**	**140°C**
Glyc	4.94	4.99		**50%**	39.59	21.04	9.23
				60%	39.59	21.04	9.23

From the tables above it is noted that the vapour was rich in methanol in all scenarios (see Appendix B.7 for more detailed tables). Methanol would turn into vapour although an appreciable amount of methanol remained in the liquid product stream exiting the reactor. Only with the large methanol to oil ratio (20:1) does an appreciable amount of methanol vapourise from the liquid mixture. A separate study which includes fugacities and using non ideal behaviour of vapour and liquid can give additional understanding of the behaviour of methanol.

5.6 Conclusion

The test rig used in this project proved challenging to operate and control. The commissioning runs were helpful in guiding the experimental runs which concentrated on the effects of reboiler temperature and packing on oil conversion. The experimental trials did not yield high levels of conversion of sunflower oil to FAME biodiesel despite the belief that the configuration of the test rig had many features which promote high biodiesel production.

6 Analysis of Results and Discussion

6.1 Introduction

In the previous chapter the experimental runs were presented. In this chapter the analyses of these runs are discussed in order to evaluate the performance of the prototype test rig. The evaluation focuses on the functionality and the feasibility of the prototype as built and its configuration during the experimental runs. Factors which are thought to affect conversion, such as temperature, packing type and height, residence time and flowrates are analysed.

In order to check further the operability and feasibility of the test rig other issues were also considered namely: methanol in the product stream, the reverse reaction and comparison with findings in the literature. This will in turn give a comparative view on whether or not the test rig and its configuration have a place in biodiesel production industry. Other external factors need also be considered such as the use of pure sunflower oil as opposed to used oil which could result in further complications.

6.2 General Results

The temperature runs and alternate configuration runs consisted of 14 experimental runs. Only results from the steady state operation of the test rig were considered. Steady state conditions also ensured that the liquid level in the pre-reactor had reached or was at the desired level. A period of 20 minutes was allowed to pass before the first sample was taken and more time was given to ensure that the FAME biodiesel, from the primer mix, in the packing and reboiler exited the test rig thus allowing the samples collected to be more representative. The samples taken from the pre-reactor and the reboiler corresponded to the same “portion of liquid” flowing through the reactor. So pairing a sample taken at 20 minutes from the pre-reactor and comparing it to a sample taken at 40 minutes from the reboiler it was possible to compare the conversion of the liquid feed at entry and product stream at the exit of the test rig. This was done for the entire range of results. This procedure excludes the 20 minute reboiler sample and the 180 minute pre-reactor sample from all the runs.

The biodiesel conversions were calculated using the viscosity chart mentioned earlier in Section 4.5.1. The molar ratios were calculated using the difference in level in the feed containers before and after each run. Although the pumps were calibrated prior to each run to deliver a 3:1, methanol to oil ratio, due to the extended period of each run flow variations occurred which resulted in the difference in molar ratios. The pre-reactor residence times were calculated from the average liquid level height over the run and the volume of the pre-reactor (Appendix D.1). The volume of the reboiler was 1.38*l*. The delta or change in conversion (Δ Conv.) was calculated by averaging the conversions in the run and then calculating the percentage increase in conversion. The average difference (Avg. Diff.) was found by subtracting the pre-reactor conversions from the overall conversions from all the samples in a specific run and then averaging the calculated differences.

The summarised results from the 14 experimental runs were grouped into two tables according to increasing temperature. Runs T9 and T10 were kept separate because a different test rig configuration was used, in that the reboiler residence time was reduced. The following tables (Table 6-1 & Table 6-2) are presented in order to identify the relationship among the results and arrive at reasonable conclusions.

Table 6-1 Summarised results from experimental runs

Run	Temp (°C)	Meth Weight %	Molar Ratio	Flowrate l/hr	Pre-React. Conv. %	Overall Conv. %	Visc. 40°C	Δ Conv. %	Avg. Diff. (%)	Total Res. Time (min)
T7	70	0.76	3.0	3.2	57.5	60.9	10.6	5.5	3.4	90
T8	70	0.76	3.1	3.2	60.5	63.7	10.0	4.8	3.1	89
T1	90	0.99	4.5	4.0	75.0	82.4	6.9	9.0	7.5	69
T2	90	0.76	3.8	3.9	53.6	66.7	9.4	19.6	13.2	77
T3	90	0.76	4.0	4.7	53.8	59.8	10.8	9.9	6.0	63
P1	**90**	**0.76**	**3.0**	**4.5**	**56.1**	**63.5**	**10.0**	**11.5**	**7.4**	**57**
P2	**90**	**0.76**	**3.0**	**4.3**	**53.7**	**61.4**	**10.5**	**12.5**	**7.6**	**59**
P4	**90**	**0.76**	**3.2**	**3.6**	**65.9**	**66.8**	**9.4**	**1.1**	**0.8**	**78**
T4	110	0.76	3.0	4.5	54.9	59.6	10.8	7.8	4.7	63
T6	110	0.76	3.1	3.8	54.4	63.2	10.1	13.7	8.7	79
P3	**110**	**0.76**	**3.1**	**3.4**	**60.2**	**65.7**	**9.6**	**8.2**	**5.4**	**84**
T5	140	0.76	3.1	4.5	53.4	59.4	10.9	10.0	5.9	63

Table 6-2 Summarised runs of experiments with modified reboiler

Run	Temp (°C)	Meth Weight%	Molar Ratio	Flowrate l/hr	Pre-React. Conv. %	Overall Conv. %	Visc. 40°C	Δ Conv. %	Avg. Diff. (%)	Pre-React. Time (min)
T9	90	0.76	3.0	4.5	49.1	58.5	11.1	16.0	9.4	24
T10	Amb.	0.76	3.0	5.3	54.0	62.1	10.3	12.8	7.9	12
	30	0.76	3.0	5.3	55.3	60.9	10.6	9.0	5.5	12
	40	0.76	3.0	5.3	63.2	65.3	9.7	3.2	2.1	21
	50	0.76	3.0	5.3	61.4	69.2	9.0	11.2	7.8	23

The overall conversions were not as high as anticipated. The molar ratios were not all as per the desired stoichiometric proportion of the reaction and certain liquid level problems were recorded. The operability of the test rig seemed to be problematic under the chosen configuration although the design does offer the ability to physically remove and alter the configuration of the test rig. The test rig was new and was never used before for experimentation.

6.3 Temperature

6.3.1 Overall Conversion

Temperature Runs

Use of different temperatures was expected to have a significant influence on the sunflower oil conversion. Four different temperatures were used in the experimental runs, namely: 70°C, 90°C, 110°C and 140°C. The following figure is a representation of the various overall conversions achieved at the four temperatures.

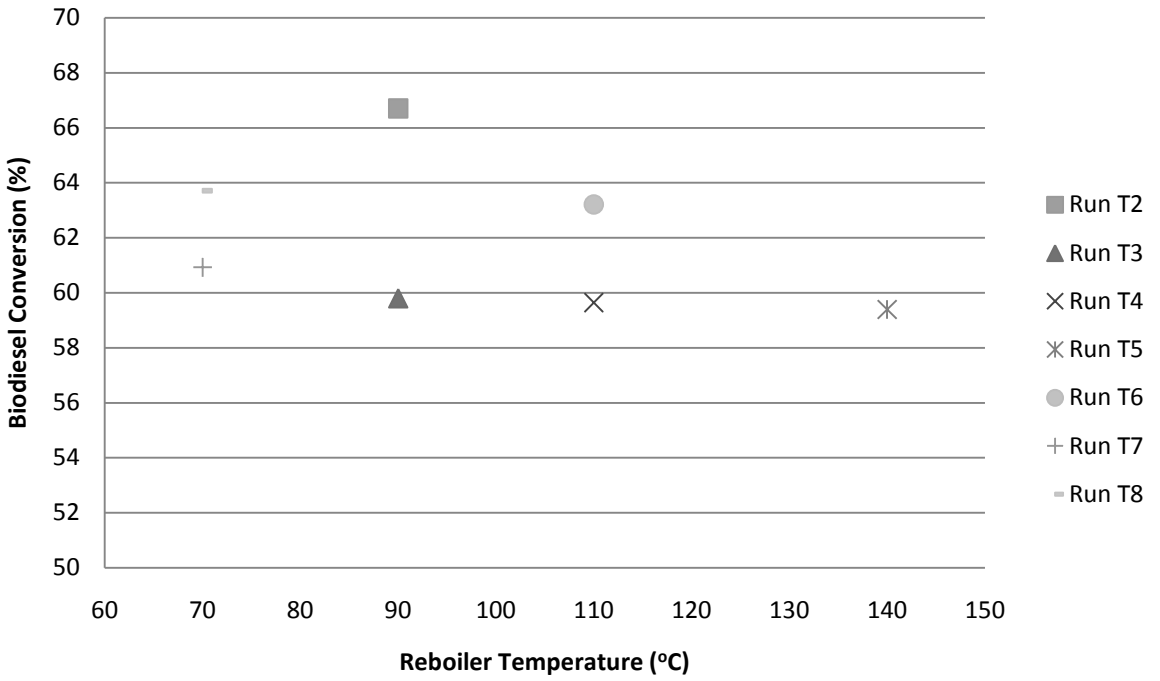

Figure 6-1 Biodiesel conversion as a function of temperature for selected runs

Only the experimental runs where a set reboiler temperature was used were included in the above figure (Figure 6-1). Run T1 was excluded because of the extreme molar ratio used (4.5:1). Run T9 and Run T10 were also excluded because of the use of different reboiler temperatures within the same experimental run. In comparison, the experimental runs in Figure 6-1 had similar molar ratios and similar test rig configuration and packing.

On the basis of Figure 6-1 conversion decreased moderately with increasing temperature. It can also be added that within the range of temperatures considered, temperature does not influence the overall conversion significantly when using the reboiler as designed, although as mentioned above there is consistent but small decrease in conversion with increasing reboiler temperature. Molar ratios of between 3.0:1 and 4.0:1 were used with no signs of an effect on conversion at different temperatures. At the reboiler temperature of 90 ^{o}C, Run T2 having a molar ratio of 3.8:1 produced a rather high conversion compared to the low conversion of Run T3 with a molar ratio of 4.0:1 at the same reboiler temperature of 90 ^{o}C The remaining experimental runs shown in Figure 6.1 have molar ratios of 3.0:1 and 3.1:1

Packing Runs

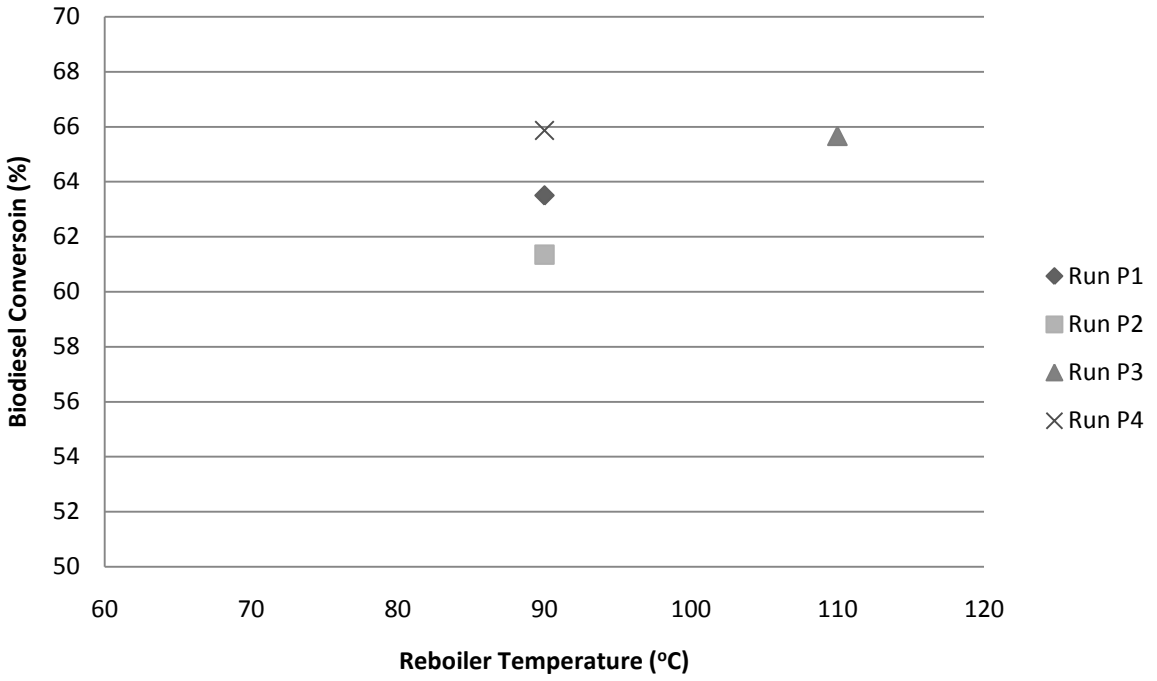

Figure 6-2 Packing Runs and conversion at specific temperatures

Runs P1 and P2 operated with a different primer mix than Runs P3 and P4. Utilising the same primer mix (Runs P3 and P4) conversion at a reboiler temperature of 90^{o}C was higher than conversion at 110^{o}C (Figure 6-3). The fact that Run P3 has a greater conversion than Runs P1 and P2 will be discussed later. Run P4 produced the highest conversion from all the runs performed; it did however have a greater methanol to oil ratio, 3.2:1.

6.3.2 Increase in Conversion

When considering the increase in conversion it is essential to compare runs having similar pre-reactor conversions and molar ratios. As it was found experimental runs with a high molar ratio would generally produce high sunflower oil conversions (Run T2). More importantly is that experimental runs with low pre-reactor conversions would yield large increases in conversions (Run T9). Although this shows the functionality of the reboiler it was not possible to identify at which conditions the reboiler could run at its optimal level, nor which temperature created a consistent increase in conversion.

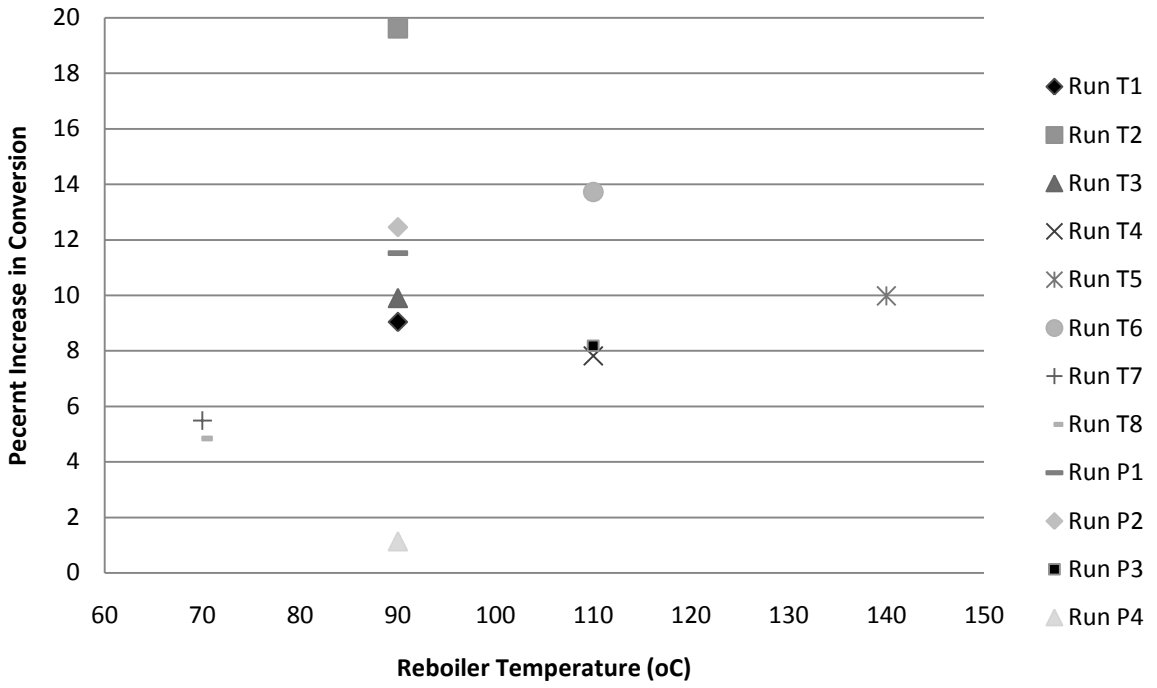

Figure 6-3 Increases in conversion at specified temperatures for selected runs

Of interest are Runs T6 and T4 operated at reboiler temperature of 110^{o}C (Figure 6-3). These runs both had very similar pre-reactor conversions yet different percent increases in conversion from the pre-reactor to the reboiler. The molar ratio of Run T6 is slightly smaller than Run T4, which meant less methanol would vapourise and hence a smaller increase in conversion, however this was not the case as the difference in molar ratio was not regarded as significant. The same can be said for Runs T2 and T3 which have molar ratios of 3.8:1 and 4.0:1 but significantly different percent increases in conversion from the pre-reactor to the reboiler.

The magnitude of the molar ratio is secondary and has less influence, in creating a substantial increase in conversion. As is also evident the effect of temperature was also minimal, as no consistent trend was found other than to say that at temperatures of 90^{o}C and above the increase in conversion was greater than at lower temperatures. Of more importance is the correct flowrate to the reboiler and operating the reboiler at its optimum operability range. The ideal flowrate is explained later. Undoubtedly if there is more methanol at the ideal flowrate the increase in conversion will indeed be greater as is evident with Run T2.

6.4 Packing and Primer Mix

The packing used in the test rig column was altered during the last 4 runs. The primer mix was also changed during the last two of the four runs. The packing was altered from marbles, (combined surface area of 167289.8mm^2), to Raschig Rings (combined surface area of 217272.5mm^2). This translated to an increase in surface area of *23%*. The primer mix was changed from 1*l* oil, 1*l* biodiesel and 126*ml* methanol to 1.5*l* oil, 0.5*l* biodiesel and 189*ml* of methanol.

6.4.1 Overall Conversion

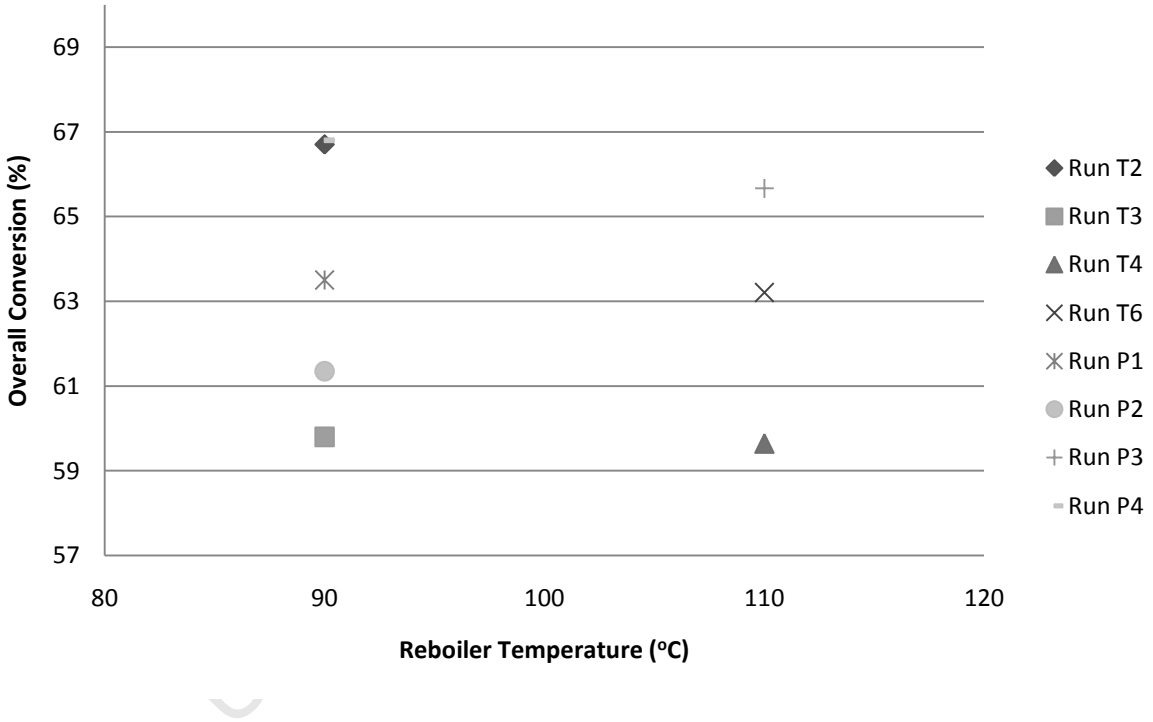

Figure 6-4 Marbles and Raschig Ring packing comparison using new primer

From the 90°C reboiler temperature runs it is evident that the change in packing produced higher sunflower oil conversions. With just the new packing Run P1's conversion was higher than the conversion achieved in Run T3. It must be noted that the molar ratio of Run T3 was greater than stoichiometric. If one considers a subsequent run which incorporated the new primer at 90°C (Run P4), overall conversion was on par or higher than conversions achieved in Runs T2 and T3 (despite of the benefit of high molar ratios experienced by T2 and T3). The new primer allowed for a more stable liquid level in the pre-reactor which caused an increase in volume and hence residence time.

Similarly in Run P3, the addition of the Raschig rings as well as the new primer mix resulted in an increase in conversion when operating at a reboiler temperature of 110^{o}C. The overall conversion was however still lower than the conversion achieved at reboiler temperature of 90^{o}C. However what cannot be fully understood in the above Figure 6-4 is how different molar ratios seem to cause little affect on overall conversion under the given test rig configurations.

6.4.2 Increase in Conversion

It can be expected that a large surface area of packing created by the Raschig Rings would assist sunflower oil conversion. The increase in conversion would be greater at greater temperatures. This would occur because the higher temperatures would cause more methanol to vapourise and condense on a greater surface area, provided for by the Raschig Ring packing.

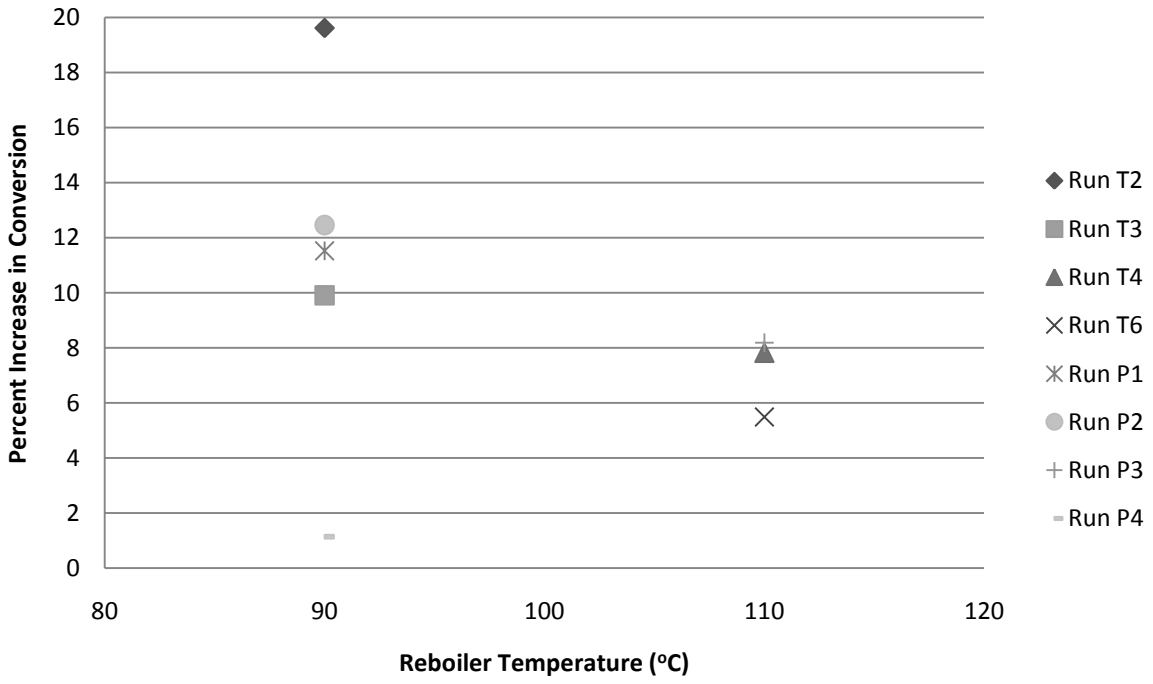

Figure 6-5 Increase in conversion using Raschig Rings packing with new primer at specific temperatures

Runs P1 and P2, as well as P3, produced higher sunflower oil conversions compared to the Marble Packing alternatives (Figure 6-5). The discrepancy with Run T2 will be discussed later. It can therefore be concluded that the Raschig Rings as well as the new primer mix contributed to an increase in sunflower oil conversion.

Run P4 is interesting because it offered the greatest overall conversion, yet had the smallest percent increases in conversion from the pre-reactor to the reboiler. All other runs, despite the large percent increases in conversion, were not able to reach the overall conversion of Run P4. This could mean the rig was operating at its optimal configuration considering that no meaningful percent increase in conversion from the reboiler occurred. Even with the added surface area of the Raschig Rings the increase in conversion was negligible.

It is evident that if the conversion is low when entering the reboiler, the reboiler will compensate and assist with the conversion reaction. The overall conversion is however limited and does appear to reach a ceiling; residence time (Run P4) and molar ratio are factors which may need to be investigated further (Run T1). The reboiler can assist in achieving a higher conversion as in T1 but would require a higher molar ratio.

6.5 Residence Time and Flowrate

The residence time in the pre-reactor was variable. The residence time in the reboiler was designed to be a variable by adjusting the hydraulic leg. For all the reported runs except T9 and T10, the reboiler volume remained fixed; therefore residence time was only dependent on liquid flowrate. Figure 6-6, below, illustrates the recorded flowrates with the recorded pre-reactor residence times. Run T9 was considered because the level in the pre-reactor remained consistent whereas Run T10 pre-reactor level fluctuated too greatly to be considered.

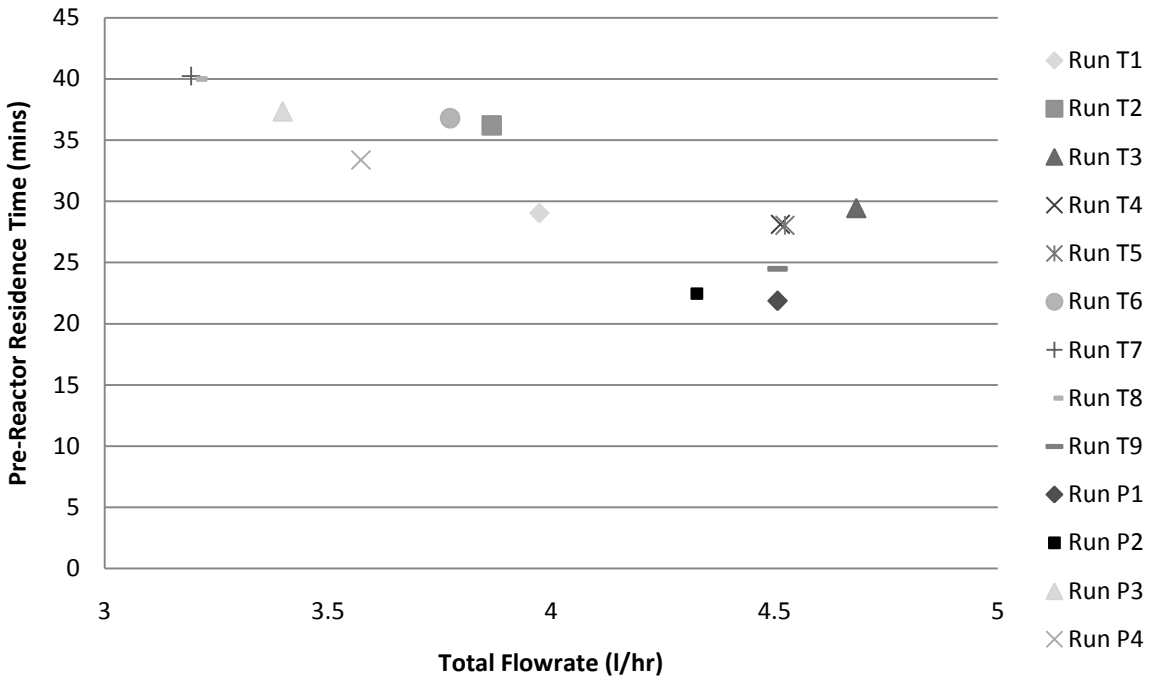

Figure 6-6 The residences times in pre-reactor with varying flowrate

In general residence time and flowrate would be a linear relation. However, when considering the test rig this was not the case. The system operated in a dynamic fashion due to the change in viscosity as the liquid mixture flowed through the column. The pumps were set at a constant rate and a band of liquid level height of operability was selected.

From the batch reactions it was understood that the greater the residence time the greater the conversion would be. As is evident from the above graph the largest residence times occurred between 3.2*l/hr* and 3.9*l/hr*.

6.5.1 Conversion

Pre-Reactor

Various aspects of the pre-reactor were analysed. These were the residence, time the molar ratio and the conversion achieved in the pre-reactor. The following graph illustrates these three factors.

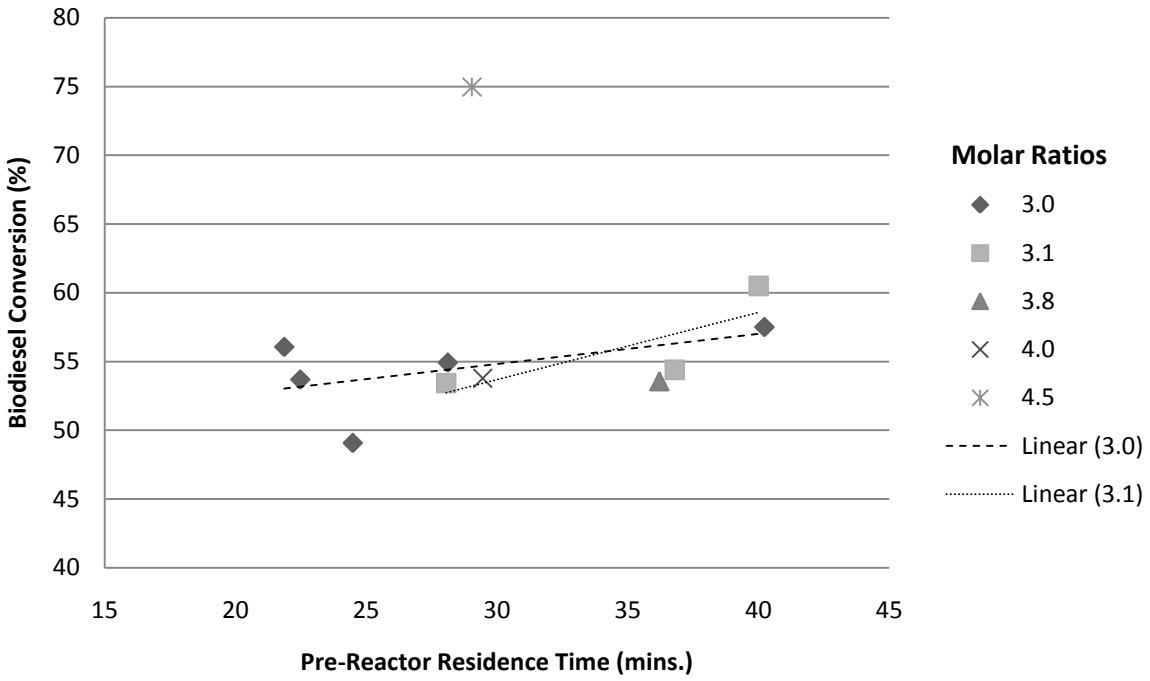

Figure 6-7 Different molar ratios and residence time for pre-reactor conversion

Trendlines were drawn through the results from experimental runs with molar ratios of 3.0:1 and 3.1:1. As can be seen from Figure 6-7, an increase in residence time meant an increase in biodiesel conversion. This trend compares favourably with the results from the stoichiometric batch runs. However, the extent of conversion is not comparable. Operating within the design specification of the test rig which has a 30 minutes residence time range, a maximum of 55% conversion was achieved compared to the batch process which yielded an average of 73% conversion of sunflower oil. The molar ratio of 4.5:1 produced a far greater conversion than any of the other runs; however this can be attributed to its super-stoichiometric ratio. It is evident from this that the current configuration of the test rig does not allow higher conversions of biodiesel to be achieved.

Experimental runs with molar ratios of 3.8:1, 4:1 and 4.5:1 showed that higher conversion was possible from a lower residence time. However, allowing the experimental run with a molar ratio of 3.8:1 the benefit of a longer residence time, conversion improved and became similar to the experimental run with molar ratio of 4.0:1. Experimental runs with molar ratios of 3.8:1 and 4.0:1 were identical except for the molar ratios and resulting flowrate. These experimental runs and the relevance to the residence times were further examined below.

If one considers a similar graph to Figure 6-7 (see figure below) with however the total residence time which includes the packing and reboiler residence time (Appendix D.1), certain trends become visible. The 4.5:1 molar ratio was omitted because of its lack of compatibility in this explanation, owing to its large super-stoichiometric ratio.

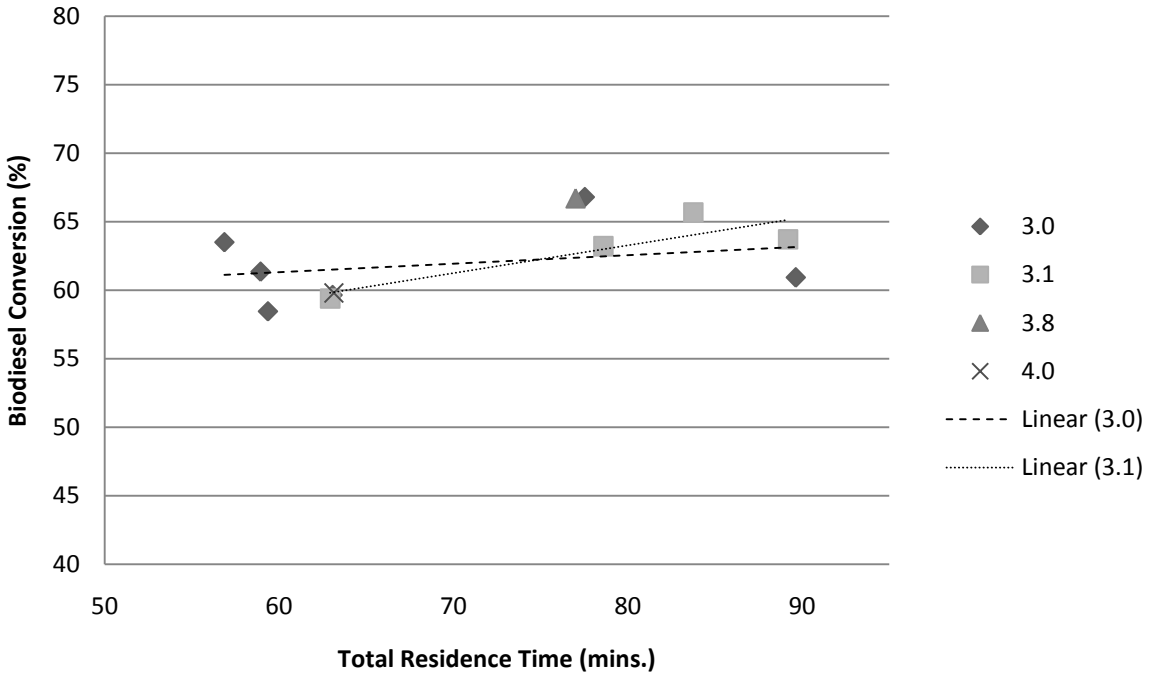

Figure 6-8 Overall conversion and residence time of different molar ratios

What is evident from the above overall conversions and overall residence times, is that if one considers the molar ratio 3.0:1 data points, the test rig seems to have reached its maximum operability. Therefore, at those specifications (regardless of changing the temperature and packing) the rate of reaction has essentially become insignificant. In comparison, when considering the molar ratio 3.1:1 data points (steeper trendline), it shows that if more residence time is made available, conversion will proceed until it reaches its limit. This is justified as the ratio is above stoichiometric and will therefore drive the forward reaction.

Temperature

The only data points excluded from Figure 6-9, below, were from Runs T1 and T10 because of their excessive molar ratio and mix of temperatures, respectively.

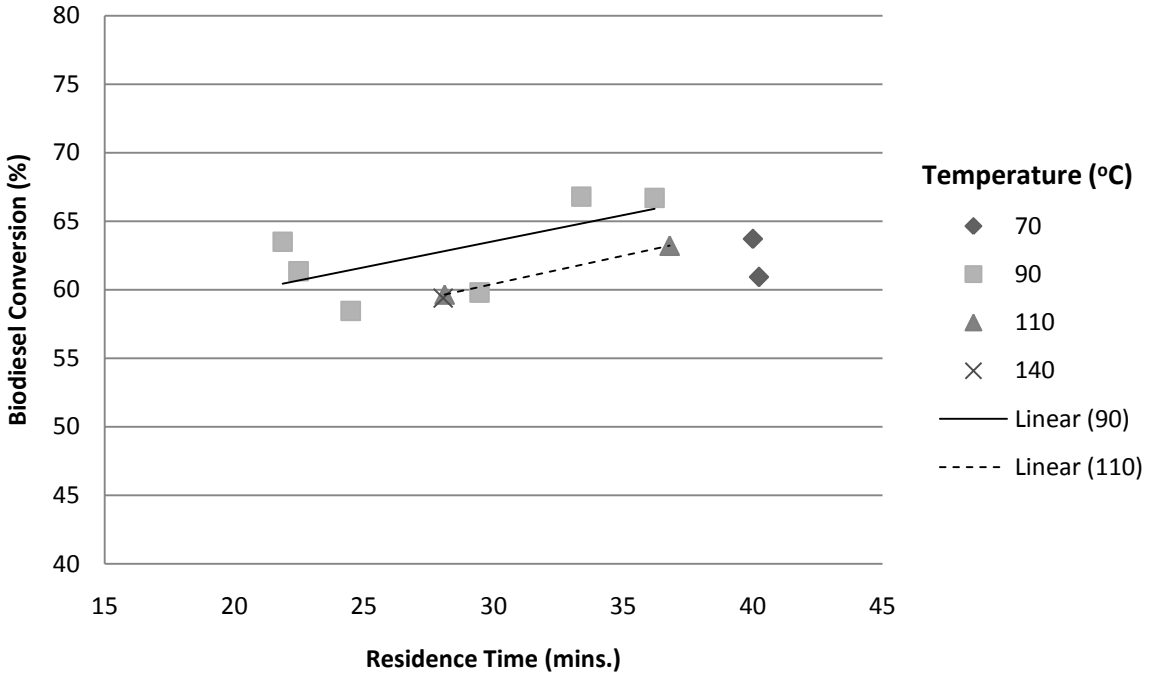

Figure 6-9 Pre-Residence Time and Overall Conversion

The 90°C run offers greater conversion at a smaller residence time in comparison to the 110°C as well as the 70°C and 140°C runs. It should be noted that with a high pre-reactor residence time, in the range of 40 minutes, the 70°C run performs as well as some of the 90°C runs, which in fact have higher molar ratios. This is interesting in terms of energy costs. One can either build a larger volume and operate at lower temperature, or have a smaller volume at higher temperature, depending on what is viable.

Packing and Primer Mix

If we consider the two results in excess of 66% biodiesel conversion giving similar overall conversion: the one point was generated using marbles as packing and a molar ratio of 3.8:1. The other point was achieved 5 minutes faster using Raschig Rings and the new primer mix with a molar ratio of 3.2:1. Despite the above differences, the extent of conversion reached a

ceiling value which is more strongly attributed to the configuration and properties of the test rig. However, even the altering of the configuration and properties of the test rig, has its own unfavourable limitations and ceiling values in terms of conversion and, therefore feasibility of the unit.

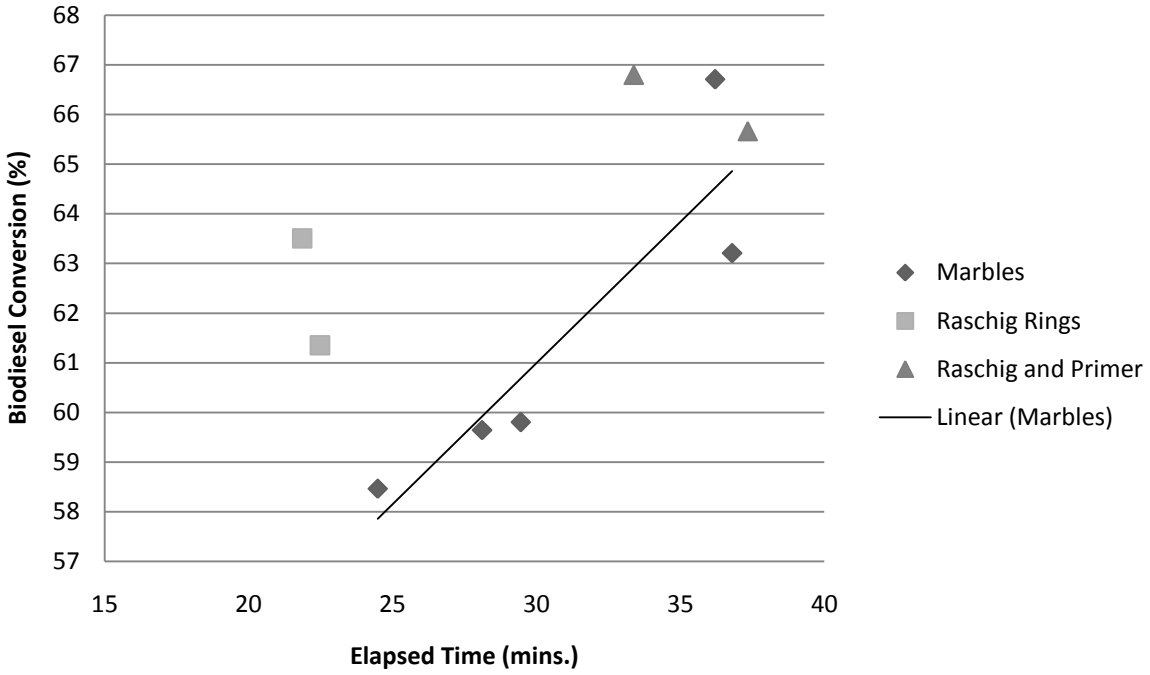

Figure 6-10 The conversion of various runs with focus on packing and primer

6.6 Flowrates and Liquid Level Height

The residence time and liquid level height were seen to have a dynamic relationship with conversion. During the construction phase as well as the operation stages of the test rig the residence time of reactants was of extreme importance. Consideration of the results explained in the previous chapter makes the feasibility of the test rig as a useful reactor questionable. However putting the extent of conversion on one side the test rig provided useful information in understanding factors influencing biodiesel conversion. The quality of diesel produced in the test rig is still regarded as good grade biodiesel.

The test rig operated under steady state successfully although, under steady state conditions there was a dynamic test rig behaviour resulting from the effect of many variables interacting together. The main factors were the residence time, conversion, viscosity and feed flow rate. The liquid level height in the pre-reactor relates to the residence time. The residence time in turn is dependent on the feed flow rate and viscosity in the pre-reactor. Conversion is dependent on the residence time and directly affects the viscosity. As viscosity is directly related to the residence time it is evident that conversion and residence are a function of each other. The dynamic behaviour of the test rig can be explained as follows: If conversion is low the viscosity would remain high and the level in the pre-reactor would increase (at a set feed flow rate). This would increase the residence time. Once a specific liquid level had been reached the feed flow would stop. The feed flow would commence again once the liquid level in the pre-reactor dropped as a result of a high residence time, a higher conversion and a reduced viscosity. The decrease in viscosity meant flow would increase and the liquid level would begin to drop at a higher rate.

Generally the level in the pre-reactor was difficult to maintain because of the above mentioned dynamic relationship. This problem was further amplified by two factors caused by the feed pumps. Firstly the feed pumps were calibrated prior to the run to ensure a preset molar feed ratio was maintained. The pumps could therefore not be tampered with during the test run i.e. increase or decrease the pump rate. Secondly in order to ensure the test rig remained simple and cost effective; no level controller was incorporated in the design. The feed pumps were already the result of a modification to the test rig when it was realised that constant feed could not be maintained using gravitation and feed tanks. Without a level controller the level in the pre-reactor was controlled by the rig operator which introduced possible human error.

Since flowrate had a direct effect on residence time it is important to analyse the effect of flowrate on the overall conversion. This is depicted in the graph in Figure 6-11 below.

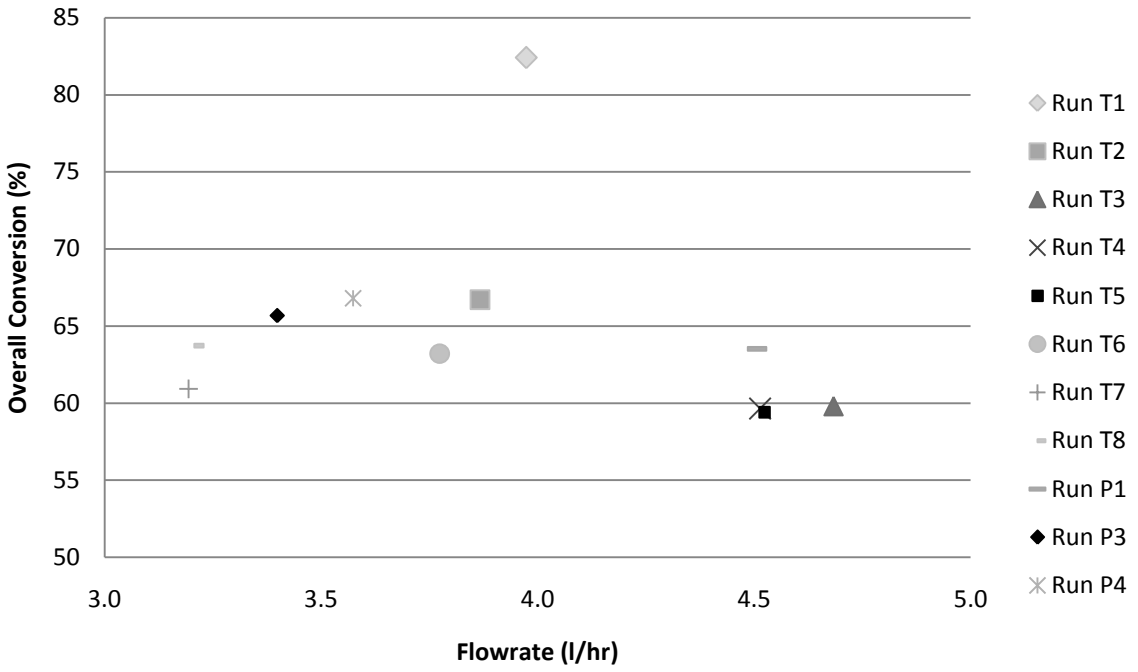

Figure 6-11 Flowrates and Overall conversions for all runs

It is evident from the above graph, with the exception of Run T1 (which had a high molar ratio) overall conversion was high and decreased with liquid flowrate (see also Figure 6-6). The experimental runs with liquid flowrate of between 3.4*l/hr* and3.9*l/hr* returned the best conversion. Based on this it is fair to assume for this series of experiments the flowrate and resulting residence time played role in overall conversion. Residence time could therefore be the basis of future experiments that could be performed on the unit; undoubtedly with an improved liquid feed system.

6.7 Reverse Reaction

The increases in conversion observed between the pre-reactor and the final product were thought to possibly have been small because of the reverse reaction occurring in the reboiler. This seemed feasible as mentioned previously, viz. that the removal of unreacted or excess methanol, by means of heating, in the presence of a catalyst could cause the reverse reaction. This would mean that the heating would cause a shift in the equilibrium and biodiesel would begin to return into methanol and triglycerides.

On the basis of consideration of Runs T9 and T10 it is evident that the reverse reaction did not happen in the reboiler. All results at steady state displayed an increase in conversion from the pre-reactor to the reboiler (Figure 5-18 & Figure 5-19). The increase in conversion can however be attributed to conversion of the biodiesel occurring in the packing. This is the case if one looks at Figure 5-22 and Figure 5-23 where there is minimal time recorded in the reboiler. Overall conversion was in the region of overall conversion from other runs (Table 6-1 and Table 6-3) and therefore it can be concluded that the reverse reaction was not occurring.

Table 6-3 Conversion and increase in conversion for runs performed with minimal Residence time in Reboiler

Temperature	Pre-Reactor Res. Time	Conversion	Incr. Conversion
40	21	65	3
50	23	69	11

This is not to say that the reverse reaction was not occurring at all in the reboiler because conditions were in fact favourable for the reverse reaction. This could have occurred with run P4 as the increase in conversion was negligible and the extended residence time did not increase conversion. Therefore either the reverse reaction was occurring in that specific run or once again the ceiling of this test rig configuration was reached showing the limitation of the capability of the test rig.

6.8 Methanol in Products

It can be assumed that the majority of the excess or unreacted methanol exited the reactor in the product solution. This can be substantiated by the mass balance calculations performed where minimal loss of mass was reported over the entire run as well as the minimal recovery of methanol in the condenser.

Raoult's Law calculations also confirm that methanol reported in the product stream. It is important to note that these calculations merely substantiate the presence of methanol in the product stream where the mass balance calculations justify its presence in the product stream. Raoult's Law calculations assumed ideal mixture and ideal vapour behaviour and used input

values and bound by specific input criteria. The calculations did report methanol in the product stream under all Scenarios (Table 5-3, Table 5-4 and Table 5-5). From the literature, where current reactive distillation methods are investigated, methanol is always reported in the product stream. It can be concluded that there is an affinity for methanol to remain in the product stream at the temperatures tested under the current project. This would have a negative effect on the internal methanol recycle and high sunflower oil conversion. In order to successfully remove large amounts of methanol from the product stream a large ratio of methanol to oil was required, as is evident in Scenario 3 which had a ratio of 20:1. However, methanol would still be found in the product stream. Excessive removal would also drive the reaction to the left and therefore a balance must be found.

The feasibility of reactive distillation, especially the ability to separate methanol from the product stream in the reboiler would thus require serious analysis if the prototype as built were to be commissioned for more runs using methanol to oil feed ratios of less than twice stoichiometric.

6.9 Comparison with published work

The final investigation was aimed at establishing the competitiveness of the test rig when compared with current reactive distillation methods described in the literature. As previously stated however the unit did not return high conversions of biodiesel based on its current specifications and configuration. From He et al. (2006) conversion ranged from 78% (molar feed ratio of 3.0:1) to 95% (molar feed ratio of 4.0:1), see (see Table 2-1 and Table 2-2).

The best run achieved by the test rig occurred when a molar feed ratio of 4.5:1 was used giving a conversion of 82%. In the literature a 92% conversion was achieved using similar operating conditions. This finding points again to the fact that the test rig configuration had limitations. Similarly, the test rig's conversion operating under stoichiometric molar feed conditions returned conversions averaging 60%, which were substantially lower than the literature value of 75%. The literature values were taken from He et al. (2006). The test rig's conversion was also compared to the conversion from the batch trials and found to be significantly lower.

He et al. (2006) did not seem to have any problems with the reverse reaction. The reboiler in their runs seemed to perform in a range where the reverse reaction would be favoured. However no report on the reverse reaction ever occurring was made. A mention is however made of a "catalyst killer" used in the samples. They made use of a catalyst killer for their samples but not in their reboiler, suggesting the reverse reaction occurring was not a problem.

A mass balance analysis over the reboiler using the conversion obtained from the experimental samples reveals that the methanol to oil ratio in the reboiler was not as high as reported in literature. Literature reported values in the regions of 15-20:1 (He et al. 2006). This means that the internal methanol recycle envisaged was not offering a high enough molar ratio. The below table illustrates the various reboiler methanol to oil ratios from all the runs. The table was calculated from the overall volumes of feedstock and product used over a run and may therefore have fluctuated over the duration of the run.

Table 6-4 Methanol to reboiler ratio in reboiler

Run	Reboiler Molar Ratio Methanol to Oil	Conversion
T1	11.8	82.4
T2	5.4	66.7
T3	5.6	59.8
T4	3.1	59.6
T5	3.2	59.4
T6	3.3	63.2
T7	3.0	60.9
T8	3.3	63.7
T9	3.0	58.5
T10	3.1	64.4
P1	3.0	63.5
P2	3.1	61.4
P3	3.4	65.7
P4	3.6	66.8

The test rig did not achieve product conversions found in the literature. The test rig configuration could be the reason for the low conversion. The unit was however designed

with a large set of configuration options which could be implemented in future test runs to increase conversion.

6.10 Conclusion

The rig did not perform as well as initially expected from the batch reactions. Conversion percentages comparable to those found in literature were not achieved. The test rig's current configuration and specification set-up was used to carry a series of experimental runs after a series of commissioning tests. The operability of the unit, although troublesome at the start, improved with the various runs. The following findings were derived from the experimental work on the test rig:

- Increase in reboiler temperature corresponded to a decrease in sunflower oil conversion
- The increase in surface area of the packing coupled with a new primer mix resulted in increase in oil conversion
- Residence time, which was strongly tied to the liquid flowrate through the columns and liquid level height (see Chapter 6.2 & 6.5) had the largest influence on sunflower oil conversion

Overall sunflower oil conversion was found to be in the range of 50% to 65% with the exception of Run T1 where a large methanol to oil ratio was used. Residence time was found to have the greatest influence on conversion in the test rig. Residence times were divided into the pre-reactor residence time, the column residence time and the reboiler residence time. The pre-reactor residence time was closely monitored because of the changes in liquid level height and its effect on conversion. The inclusion of a different packing increased the residence rime in the column which resulted in an improved conversion.

Temperature of the reboiler had a positive improvement on conversion although the same effect can be achieved by introducing a longer residence time. A similar argument can be said for the packing and primer mix. The dynamic relationship of flow, level and viscosity proved

challenging to control relying on operator intervention which meant sunflower oil conversion may have been affected.

The separation of methanol from the product stream did not occur as was first envisioned. This was substantiated by the mass balance and vapour liquid equilibrium calculations. The affinity of the methanol to remain in the liquid product was seriously underestimated because the configuration of the unit did not take advantage of the huge boiling point difference of the components in the product stream.

A conversion ceiling was reached in all experimental runs attributed to the test rig configuration. This also meant that the configuration of the test rig needed to be changed to make an attractive plant for biodiesel production. The test rig would need to be altered to obtain improved results.

7 Conclusion and Recommendations

7.1 Objectives Revisited

Biodiesel production remains a viable option for the future. Diesel engines still have a place in the industrial economy, and biodiesel can offer a solution to the ever diminishing oil reserves. Biodiesel production as a field still requires research as many methods of production are simple and inefficient. The aim of this project was to design, construct and understand a prototype for a novel method of production of biodiesel.

The dissertation had four main objectives, see Chapter 1.3.

- To develop a theoretical understanding of the chemical and physical phenomena occurring in reactive distillation of the triglycerides and methoxide in order to make FAME biodiesel;
- To present the approach to design and proceed with the construction of a prototype to produce biodiesel;
- To report on a series of experimental runs, analysing the results and determining the operability of the prototype using different operating parameters;
- To discover whether the novel configuration is feasible in terms of biodiesel production and compare it to industrial norms.

Ultimately, it was envisaged that the novel unit would become a competitive option for consideration by small and large scale biodiesel producers. The unit would also incorporate attractive features based on its simplicity and low construction and operation costs.

7.2 Conclusions

A theoretical understanding of the vegetable oil to biodiesel process was established using a literature review. The knowledge gained formed the basis where the project could proceed. The literature was extensively researched to extract the current most applicable knowledge in the field. In particular, encouraging results were found in the reactive distillation laboratory-scale work of He et al. (2006). Improving methanol efficiency should help to cut production

and energy costs. Reactive Distillation methods for biodiesel production were seen as a possible avenue to improved methanol efficiency.

The batch reactions and the vapour liquid equilibrium analyses proved to be helpful in understanding the limits and mechanics of the theory on which the design of the test rig was based, as well as the limitations of the test rig. Coupled with the literature and design calculations, an effective approach towards the design and construction of the unit was achieved. The project proved to be successful in its design and construction phase. The prototype was constructed to specification. Included in the design was the ability to change certain aspects of the test rig's configuration. A specific configuration was adopted and the experimental runs were performed on the said configuration. The unit was able to produce biodiesel on a continuous basis, although the conversion was not as high as was found in the literature. This meant that the unit did not achieve its target in terms of methanol efficiency.

The viscosity conversion chart designed and verified for the purposes of this project proved to be invaluable in the analyses, the representation of the experimental data and in determining the operability of the unit. Generally the conversions were found to be between 50% and 65%, with the column section improving the conversion achieved in the pre-reactor by +/- 10% dependant on experimental run.

The residence time, which tied into a dynamic relationship between the flowrate, viscosity of the liquid and the liquid level height, was the largest contributing factors in obtaining the highest conversion allowed by the molar feed ratio of reactants chosen. This dynamic relationship was also a major factor in operator ability to control the test rig.

An interesting observation was the inability of the reboiler to separate the unreacted methanol from the product stream. Simplified vapour- liquid equilibrium calculations confirmed that sizeable quantities of methanol should indeed remain in the liquid product if the vapour phase in the column is nearly pure methanol.

The prototype reactive distillation unit as designed and operated thus did not produce biodiesel to the required conversion under conditions of limiting methanol in the feed. Conversions were not as high as published by other researchers working at laboratory scale. Furthermore the test rig was operated on fresh sunflower oil and laboratory grade methanol. It is reasonable to assume that if the test rig operated on used sunflower oil a list of new problems would have been encountered. However, as the test rig configuration can be altered it may still be possible to achieve high conversions in future experimental trials.

7.3 Recommendations

Based on the conclusions drawn above concerning the design, construction and commissioning of the prototype, and the test work done with it, the following recommendations are made:

1. In terms of operability of such a process, a more sophisticated controller can be installed to regulate reagent feed flow rates, so as to manage better the dynamic relationship of the liquid level in the column, viscosity and residence time in pre-reactor.
2. A better understanding of the vapour liquid equilibrium needs to be established and the relationship of the reactants and products in the reboiler better understood. The assumption of ideal vapour and liquid needs to be re-examined, so as to understand the behaviour of methanol in the product stream. Once this is understood steps can be taken to adapt the rig accordingly. One feasible option, looking at the increased sunflower oil conversion when different packing was used (Raschig Rings) would be to increase the reboiler vapour space by extending the column. A permanent condenser could also be attached to the design to continuously withdraw methanol out of the mixture in the reboiler. This could then be fed back into the pre-reactor as found in the literature to increase conversion. Based on what was found by computer modelling, if the internal methanol recycle was increased, the methanol separation in the reboiler could prove to be feasible. The test unit should then be running closer to the conditions reported by He et al. (2006).
3. The reverse reaction should also be investigated. It is evident that conditions in the reboiler favour the reverse reaction although the experimental runs showed no conclusive proof of the reverse reaction happening. Further testing is encouraged, looking at decreasing

the reboiler liquid volume (and hence residence time) and increasing the reboiler vapour. This could further minimise the potential for the reverse reaction to occur. Experimental runs including injecting a catalyst killer to prevent the reverse reaction being catalysed should also be explored.

4. Further experiments and repeat runs could be performed. This could further validate the findings of this project as well as provide more data points.

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Appendices

A Appendix A – Design Calculations

A.1 Marble and Raschig Ring Surface Area

The surface area of the marble packing was done in a spreadsheet (Table A-1). The amounts of marbles as well as the diameters of the big marbles (BM) and small marbles were known (SM).

Table A-1 Calculation of the surface area of the Marble Packing

Big	Amount	33		**Small**	Amount	145
Dimension				**Dimension**		
D	25	mm		D	15	mm
Vol	8181.231	mm^3		Vol	1767.146	mm^3
SA	1963.495	mm^2		SA	706.8583	mm^2
Vol BM	269980.6	mm^3		Vol SM	256236.2	mm^3
SA BM	64795.35	mm^2		SA SM	102494.5	mm^2
Tot Vol	**526216.8**	**mm^3**				
Tot SA	**167289.8**	**mm^2**				

The surface area (SA) of the Raschig Rings was also calculated in order to compare the improvement in surface area that would be available. The dimensions of the Raschig Rings were known as well as the amount required to fill the packing space. The below table (Table A-2) illustrates the calculation.

Table A-2 Calculation of surface area of Raschig Rings

Amount	140					
Dimension						
Height	17	mm				
OD	15	mm				
ID	11					
Wall Thickness	4	mm				
SA			**Volume**			
Ext. SA	1154.535	mm^2	External	V	3004.148	mm^3
Int. Disc	190.0664	mm^2	Internal	V	1615.564	mm^3
Int. Area	587.4778	mm^2		**VR**	**1388.584**	**mm^3**
SA	1551.947	mm^2				
Tot SA	**217272.5**	**mm^2**				

A.2 **Manometer and Pressure Relief Calculation**

The maximum operating pressure was selected at *1200Pa*. The liquid of choice was biodiesel with a density of $880kg/m^3$. All that remained to build the manometer would be to calculate the liquid height that could withstand the pressure difference. The pressure inside the reactor at start was atmospheric therefore the following equation was used in the pressure relief and manometer calculations.

$$\Delta P = \rho g \Delta h$$

Equation 10

Where: ΔP – change in pressure; ρ – density of substance; g – gravitational acceleration taken as $9.81 m/s^2$; Δh – change in height..

A.3 **Volume Calculation**

The below spreadsheet (Table A-3) was used to calculate the maximum operating volumes for the respective section of the unit. The dimensions of the pipe were set by the manufacturer as the pipe was bought to those specifications for pricing reasons.

The additional height added to the column was done to provide variability in packing height and packing type. For construction purposes the various heights were also increased as is evident with the unit's drawings (Figure 3-2, Figure 3-3 and Figure 3-4).

Table A-3 Spreadsheet used to calculate required volumes

Maximum Flowrate					
5	l/hr				
Desired Res. Time					
Pre-reactor	0.5	hr			
Column	0.25	hr			
Reboiler	0.25	hr			
Volume			**Assumptions**		
Pre-reactor	2500	ml	Voidage	0.4	
Column	1250	ml			
Reboiler	1250	ml	Tot Column Vol.	3125	ml
Dimensions of Pipe					
ID	108.2	mm			
Wall Thick.	3.05	mm	Safety Factor	10	%
OD	114.3	mm	Add. Height- Column	100	mm
Required Section Height					
	Height (mm)	10% Height (mm)	Total (mm)		
Pre-reactor	272	27	299	mm	
Column (incl. voidage)	340	34	474	mm	
Reboiler	136	14	150	mm	

A.4 **Molecular Weights**

An analysis of a 20*ml* of sunflower oil (SFO) was performed using a GC. The analysis was performed using C_{19} as a standard. The following graph was produced

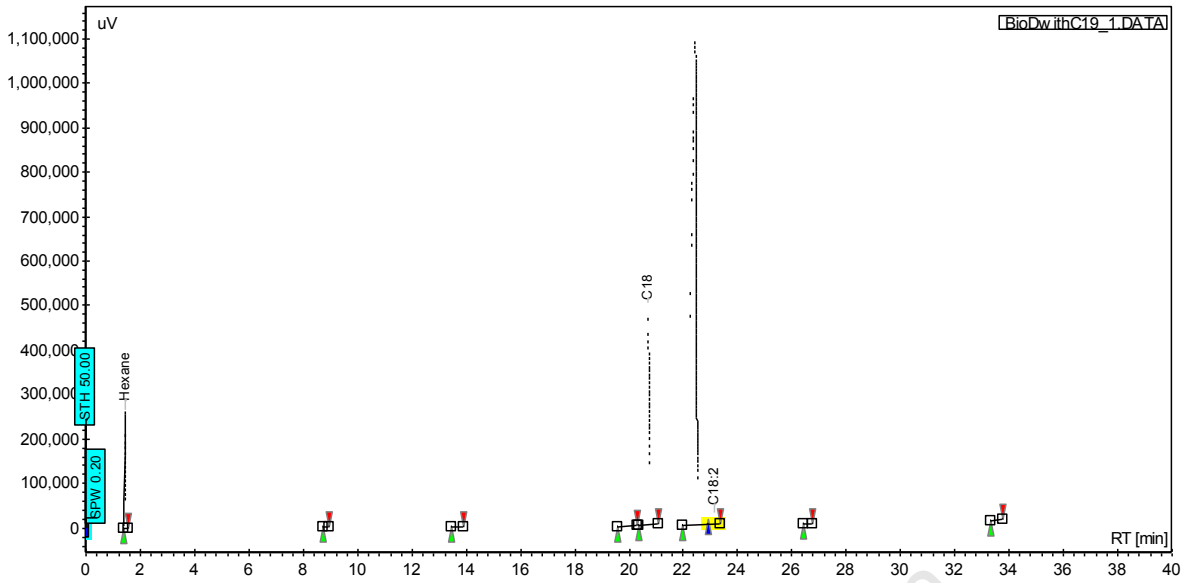


Figure A-1 Graphed produce by GC analysis

From the analysis the various percentages of the Fatty Acids in the SFO could be established. These values were taken and compared to other literature values obtained. These literature values gave their specific percentages for Fatty Acids in their SFO samples. The below spreadsheet (Table A-4) was used to illustrate and compare composition of the SFO based on Fatty Acid content.

Table A-4 Spreadsheet illustrating SFO compositions

Fatty Acid			MW	Compositions			
				O'Brien, (2004)	Marchetti et al. (2007)	Nusun (O'Brien, 2004)	GC
Myristic	C14:0	$C_{14}H_{28}O_2$	228.378	0.001	0	0	0
Palmitic	C16:0	$C_{16}H_{32}O_2$	256.432	0.07	0	0.043	0.06083
Palmitoleic	C16:1	$C_{16}H_{30}O_2$	254.416	0.001	0.0608	0	0
Stearic	C18:0	$C_{18}H_{36}O_2$	284.486	0.045	0.0326	0.047	0.05083
Oleic	C18:1	$C_{18}H_{34}O_2$	282.47	0.188	0.1693	0.604	0.24192
Linoleic	C18:2	$C_{18}H_{32}O_2$	280.454	0.675	0.7373	0.306	0.63756
Linolenic	C18:3	$C_{18}H_{30}O_2$	278.438	0.008	0	0	0
Arachidic	C20:1	$C_{20}H_{40}O_2$	312.54	0.004	0	0	0.00245
Gadoleic	C22:1	$C_{22}H_{46}O_2$	342.61	0	0	0	0.00641
Behenic	C22:2	$C_{22}H_{44}O_2$	340.594	0.007	0	0	0
Other				0.001	0	0	0

The calculation for the molecular weight of the triglyceride was performed as follows: The percentages of Fatty Acids, found from the GC analysis, where multiplied with their respective molecular weights and then added to the molecular weight of the attached glycerol molecule in order to create a good representative molecule of triglyceride. For the FAME

molecular weight the methyl group was added once again to the weighted averages of the Fatty Acids. The FFA's and Soaps were also calculated as weighted percentages. The molecular weight of the SFO was calculated by using the FFA content value of *0.06%*, which was given by the supplier, as follows:

$$(99.94\%)(MW_{TG})+(0.06\%)(MW_{FFA})=MW_{SFO}$$

Table A-5 Comparison of Molecular Weights

Component	O'Brien, (2004)	Marchetti et al. (2007)	Nusun (O'Brien, 2004)	GC
SFO	879.2356	878.7441	883.196	**878.1768**
TG	879.5956	879.1039	883.5577	**878.5359**
FFA	279.5075	279.3436	280.8282	**280.1623**
BD	293.5345	293.3706	294.8552	**294.1893**
Soaps	305.5575	305.4196	306.9042	**306.2383**

The above table (Table A-5) is a representation of the molecular weight calculated from the data provided form literature as well as from the GC analysis. The same method was used to calculate the MW from literature as with the MW from the GC analysis. As can be seen the molecular weights match those found in literature. The selected value which was used for later calculations was taken from the GC analysis values.

A.5 **Mass Balance**

The mass balance was set up on an excel spreadsheet (Table A-6). Certain factors and assumptions were inputted into the spreadsheet and results were then established. As example for display purposes the spreadsheet was set to the maximum design specifications of the rig i.e. 5*l/hr*.

Table A-6 Mass Balance input interface

INPUT			**Density**	**at 20 C**	
KOH for BD rxn	7	g/l oil	SFO	0.914	kg/l
Oil Volumetric flow	5	l/hr	Biodiesel	0.88	kg/l
Methanol/Oil Ratio	3	:1	Methanol	0.792	kg/l
Fraction FFA	0.0006				
RESULT			**Molecular weights**		
TG in	0.005200841	kmole/hr	Methanol	32.040	g/mol
MethVolumetric Flow	0.631192966	l/hr	KOH	56.110	g/mol
V/V	12.62385932	%	Glycerol	92.097	g/mol
KOH for Soap rxn	0.000874773	kg/hr	Water	18.016	g/mol
Tot KOH	35	g/hr	Oil	878.177	g/mol
			TG	878.536	g/mol
INPUT			FFA	280.162	g/mol
Pre Reactor Conv.	50	%	Biodiesel	294.189	g/mol
Interface Ratio	20	:1	Soaps	306.238	g/mol
Interface Conversion	90	%			
Reboiler Temperature	70	C			
Total Flow	**5.631192966**	**l/hr**			
	Mole		**Mass**		
Oil in	5.204	g/mol	4570.000	g/hr	
Methanol in	15.603	g/mol	499.905	g/hr	
KOH in	0.624	g/mol	35.000	g/hr	
Total	**21.430**	**g/mol**	**5104.905**	**g/hr**	

The below Table A-7 depicts the spreadsheet generated by the above assumptions.

Table A-7 Example of results produced by Mass Balance spreadsheet

MOLE		**Stream**	**mol/hr**		
Component	**1**	**2**	**3**	**4**	**5**
Methanol	15.603	7.801	44.987	0.078	44.207
KOH	0.624	0.621	0.621	0.621	0
TG	5.201	2.600	0.260	0.026	0
FFA	0.003	0	0	0	0
Glycerol	0	2.600	4.941	5.175	0
Soaps	0	0.003	0.003	0.003	0
Methyl Ester	0	7.801	14.822	15.525	0
Water	0	0.003	0.003	0.003	0
SUM (mol/hr)	21.430	21.430	65.637	21.430	44.207
MASS		**Stream**	**g/hr**		
Component	**1**	**2**	**3**	**4**	**5**
Methanol	499.905	249.952	1441.392	2.500	1416.397
KOH	35.000	34.825	34.825	34.825	0.000
TG	4569.125	2284.563	228.456	22.846	0.000
FFA	0.875	0.000	0.000	0.000	0.000
Glycerol	0	239.491	455.033	476.587	0
Soaps	0	0.956	0.956	0.956	0
Methyl Ester	0	2295.048	4360.590	4567.145	0
Water	0	0.056	0.056	0.056	0
SUM (g/hr)	5104.905	5104.891	6521.309	5104.914	1416.397

A.6 **Packed Bed**

From the Mass Balance spreadsheet it was possible to calculate the weighted density and viscosity of the liquid passing through the unit. The values were for density 896.18kg/m^3 and 0.0340$Pa.s$ for viscosity. The liquid height was taken at its maximum operability at $30cm$ and the sand particle size was taken as an average of the largest size at 0.00077m. The Packing height was set at its maximum at 26cm. A further 10cm of packing could be added if required by using the second tray support. The spreadsheet below (Table A-8) was used to evaluate and alter certain inputs in the packed bed calculation

Table A-8 Packed Bed calculation spreadsheet

INPUT							
Given	Column Diameter		0.1082	m	**Calculate**		
	Liquid Height		0.3	m	Liquid Vol.	2.758453	Litre
	Liquid Density		896.1823	kg/m3	ΔP	2637.464	Pa
	Liquid Viscosity		3.40E-02	Pa.s			
	Sand Diam.		0.00077	m	Packing Vol.	2.39066	Litre
	Packing Height		0.26	m			
	Packing Density		2500	kg/m3	**Assume**	**e**	**0.4**
u_c	**0.000175**	**m/s**					
Q	1.61E-06	m3/s					
	5.8	l/h					
				Target			
Pre R Res Time		**28.64**	Min	30	min		
Packing Res time		**24.82**	Min	15	min		

A.7 **Heating Element**

From the mass balance and using the previous assumptions made the following table (Table A-9) illustrates the mass of the various components in the various streams.

Table A-9 Weights of components calculated from Mass Balance

MASS	Stream (kg/hr)				
Component	1	2	3	4	5
Methanol	0.500	0.250	1.441	0.002	1.416
KOH	0.035	0.035	0.035	0.035	0
TG	4.569	2.285	0.228	0.023	0
FFA	0.001	0	0	0	0
Glycerol	0	0.239	0.455	0.477	0
Soaps	0	0.001	0.001	0.001	0
Methyl Ester	0	2.295	4.361	4.567	0
Water	0	0.000	0.000	0.000	0

The values above were used with specific heats from obtained from literature (Santos et al. 2005) to calculate the energy required in order to obtain above the projects requirements. The below table (Table A-10) illustrates the calculation and findings.

Table A-10 Energy requirement calculation

Component	**Methanol**	**Glycerol**	**SFO**	**BD**		
Cp_l (kJ/kg.K)	2.531	2.4	2.108056	2.108056		
Cp_v (kJ/kg.K)	1.375					
H vap (kJ/Kg)	109.8939					
T_i (K)	298					
T_{bp} (K)	337.7					
T_f (K)	453					
Stream	Q_{METH}	Q_{GLYC}	Q_{SFO}	Q_{BD}	Q_{TOT} (kj/hr)	**Q_{TOT} (kW)**
1	184.421	0.000	1492.955	0.000	1677.376	**0.466**
2	92.210	89.091	746.478	749.904	1677.682	**0.466**
3	531.747	169.272	74.648	1424.817	2200.484	**0.611**
4	0.922	177.290	7.465	1492.308	1677.985	**0.466**

B Appendix B – Conversion Calculations

B.1 Neutralisation Reaction

In order to neautralise the reaction in the samples containers water and an acetic acid solution were used. The acetic acid was obtained from Dewkist White Sprit Vinegar which was available from a local department store. The vinegar contained 6% acetic acid. The density of the vinegar was measured at 1.01*g/ml*. The density of Acetic acid was given as 1.05*g/ml* Therefore in 1*ml* of vinegar there is 0.06*ml* acetic acid or 0.063*g*

A uniform concentration of reactants was assumed there 1*l* of oil, 126*ml* of methanol and 7*g* of KOH. This was taken as the standard. The concentration of KOH in the standard solution was 0.006217*g/ml*. And in a 20*ml* sample there would be 0.1243*g* of KOH or 0.002216*mols* of KOH.

Considering the neutralisation reaction and stoichiometry 1*mol* of acetic acid will neutralise 1*mol* of KOH. Therefore 0.002216*mols* or 0.1331*g* of acetic acid would be required to the 20*ml* sample. In addition it would be advantageous to add additional Acetic acid as a safety measure so even if the molar feed ratio varied the reaction in the sample would still be killed. (The molar feed ratio would affect the sample as the KOH was premixed into the methanol prior to feeding it into the rig).

As a result the standard of 3*ml* of vinegar was selected. This amount of vinegar would allow for 0.1890*g* of acetic acid to be placed in the sample container. This value catered for required amount of 0.1331*g* as well as a precautionary amount of 0.05592*g*.

B.2 Constant

The equation supplied by the viscometer supplier in order to calculate the calibration constant at various temperatures is as follows

$$C_2 = C_1\{1 + [4000V(\rho_2 - \rho_1)/(\pi D^2 h \rho_2)]\}$$

Where C_2 – New constant ((mm^2/s)/s), C_1 – The constant of the viscometer when filled and calibrated at the same temperature ((mm^2/s)/s), V – Volume of the charge (ml), D – Average diameter of the meniscus (mm), h – Average driving head (mm), ρ_1 – Density of test liquid at filling temperature (g/m^3), ρ_2 – Density of test liquid at test temperature (g/m^3)

The constant was found using a spreadsheet and the given values displayed in the below table

Table B-1 Calculation of Viscometer constant

C_1	0.10384	(mm^2/s)/s
V	9.4	ml
D	21	mm
h	72	mm
ρ_2	0.867	g/m^3
ρ_1	0.875	g/m^3
C_2	0.10348	(mm^2/s)/s

The above equation was found to rely heavily on the density of the substances involved.

B.3 **Volume Percent to Conversion Percent**

If one assumes a 100*ml* sample containing 60*ml* FAME and 40*ml* SFO. There is a 60% FAME in the mixture. Therefore in order to prove that the volume and conversion are interchangeable one assumes 60% conversion in the following equation

$$60\%\ Conversion\ of\ FAME = \frac{N_{SFO}in - N_{SFO}out}{N_{SFO}in}$$

Considering $\rho = \frac{m}{v}$ for density and $N = \frac{m}{M_w}$ for moles

Where N – is moles, m – mass (kg), M_W – molecular weight (kg/kmol), v – volume ( ), ρ - density

Therefore

$$0.6 = \frac{N_{SFO}in - N_{SFO}out}{N_{SFO}in}$$

$$0.6 = \frac{\frac{(100ml)(\rho_{SFO})}{Mw_{SFO}} - \frac{(x)(\rho_{SFO})}{Mw_{SFO}}}{\frac{(100ml)(\rho_{SFO})}{Mw_{SFO}}}$$

$$0.6 = \frac{\frac{(\rho_{SFO})}{Mw_{SFO}}\ (100ml - x)}{\frac{(100ml)(\rho_{SFO})}{Mw_{SFO}}}$$

$$0.6 = \frac{100ml - x}{100ml}$$

$$x = 40ml$$

Therefore 60% conversion of FAME and a sample containing 60% FAME are synonymous. This is further reinforced because all samples contained no methanol or glycerol and therefore purely consisted of FAME and SFO.

B.4 **Unreacted Methanol Calculation**

The below Table B-2, represent the spreadsheet used to calculate the unreacted methanol in the stoichiometric batch reaction. The amount of methanol in a glycerol and FAME BD sample were found respectively. The amount of methanol per *ml* of each sample was found (*g/ml*); this value was then multiplied by the amount of glycerol and FAME BD present after the reaction. The two values obtained were then added and the final amount of unreacted methanol was calculated.

Table B-2 Calculation of unreacted methanol

	Glycerol	FAME BD
Sample (ml)	60	40
Beaker (g)	45.60	47.21
Before Heat (g)	113.80	76.65
After Heat (g)	108.00	76.26
Difference	5.80	0.39
Meth - *g/ml*	0.10	0.01
Amount from Reaction (*ml*)	100	1030
Methanol	9.67	10.00
	Total	19.67

B.5 **Batch Reaction for Conversion Chart**

The batch reaction was performed in a glass beaker at 60^{o}C. The stoichiometric ratio of methanol to oil was 6:1 and the methanol weight % was 0.8.

Conversion								
0.983037								
Substance	**In**				**Out**			
	Vol (ml)	**Mass (g)**	**Density**	**Mol**	**Vol (ml)**	**Mass (g)**	**Density**	**Mol**
TG	1500	1369.0	0.913	1.6	25.4	23.2	0.913	0.0
Methanol	380	296.7	0.781	9.3	191.8	149.8	0.781	4.7
KOH		11.0				11.0		
Glycerol		-		0.0	125.0	140.8	1.126	1.5
SFOBD		-		0.0	1557.5	1351.9	0.868	4.6
Total	1880	1676.7		10.8	1899.8	1676.7		10.8

The glycerol product that was separated off from the above reaction was boiled to remove all excess methanol so that the amount of glycerol could be weighed. The overall conversion obtained was 98%.

B.6 **Residence-Time in Batch Reactions**

The below Table B-3 represents the spreadsheet used to calculate the conversion achieved from three separate batch reactors. Samples were taken at a specific time, placed through the BS/U-tube viscometer. The respective viscosities were calculated using Equation 5 and their conversions from Equation 6.

Table B-3 Batch reactions data

Sample	**A**		
Time (min)	**Visc. Time (s)**	**Visc. (mm^2/s)**	**Conv. (%)**
18	128.19	13.26589	68.31915
28	115.22	11.92335	72.95816
38	112.04	11.59428	74.175
Sample	**B**		
Time (min)	**Visc. Time (s)**	**Visc. (mm^2/s)**	**Conv. (%)**
19	125.94	13.0327	69.09023
29	113.01	11.69466	73.8002
39	110.81	11.46699	74.65495
Sample	**C**		
Time (min)	**Visc. Time (s)**	**Visc. (mm^2/s)**	**Conv. (%)**
20	119.53	12.36937	71.36146
30	111.69	11.55806	74.31103
40	106.81	11.05306	76.25345

B.7 **Raoult's Law Calculations**

The Raoult's law calculations were performed using a computer program called Fortran. The Antoine Constants were found from literature and are readily available for glycerol and methanol. The Antoine constants for the sunflower oil and biodiesel were calculated from the GC analysis performed on the sunflower oil used in this project. The constants were found to be *A= 8.790932; B=1825.357; C=-157.209*. These values were calculated by taking the composition of the oil in terms of its fatty acids components and multiplying these values with the respective A, B and C constants and taking the sum (Yuan et al., 2005).

The script used in the program is presented below

```
PROGRAM Main
```

```
use Data

do i = 1,2
   do j = 1,3

      if (i.eq.1) then
         Feed(1) = 7.8!14.82
         Feed(2) = 2.6!0.26
         Feed(3) = 7.8!44.99
         Feed(4) = 2.6!4.94
      else
         Feed(1) = 9.36!14.98
         Feed(2) = 2.08!0.21
         Feed(3) = 6.24!35.99
         Feed(4) = 3.12!4.99
      end if

      if (j.eq.1) then
         Temp = 92.0 + 273.15
      else if (j.eq.2) then
         Temp = 110.0 + 273.15
      else
         Temp = 140.0 + 273.15
      end if
      write(1,*)i,j
      write(1,*)

      CALL VLE

   end do
end do




END PROGRAM



subroutine VLE

use Data

INTEGER::n,info,lwa
DOUBLE PRECISION::tol
DOUBLE PRECISION::x(10),fvec(10),wa(250)

external fcn

Totfeed = sum(Feed)

n = 10

x(1) = 0.9
x(2) = 0.9
x(3) = 0.01
x(4) = 0.9
x(5) = 0.01
x(6) = 0.01
x(7) = 0.9
```

```
x(8) = 0.01

do i = 1,8
x(i) = 0.9
end do

x(9) = Totfeed
x(10) = Totfeed/9.0

tol = 1.0d-12

lwa = 250

CALL hybrd1(fcn,n,x,fvec,tol,info,wa,lwa)


write(1,*)'info',info
write(1,*)

do i = 1,4
   write(1,*)'x',i,x(i)
end do
write(1,*)
do i = 5,8
   write(1,*)'y',i,x(i)
end do

write(1,*)'Liquid',x(9)
write(1,*)'Vapour',x(10)
write(1,*)
write(1,*)
write(1,*)'liquid Biodiesel',x(1)*x(9)
write(1,*)'liquid Sun Flower Oil',x(2)*x(9)
write(1,*)'liquid Methanol',x(3)*x(9)
write(1,*)'liquid Glycerol',x(4)*x(9)
write(1,*)
write(1,*)'vapour Biodiesel',x(5)*x(10)
write(1,*)'vapour Sun Flower Oil',x(6)*x(10)
write(1,*)'vapour Methanol',x(7)*x(10)
write(1,*)'vapour Glycerol',x(8)*x(10)

write(1,*)
write(1,*)
do i = 1,n
   write(2,*)fvec(i)
end do



END subroutine

!------------------------------------------------------------------------
----------------------------

subroutine fcn(n,x,fvec,iflag)

use Data

INTEGER::n,iflag
DOUBLE PRECISION::x(10),fvec(10),pvap(4)
```

```
!1 - Biodiesel
!2 - Sun Flower Oil
!3 - Methanol
!4 - Glycerol

!Feed(1) = 0.008985*1000.0
!Feed(2) = 0.000529*1000.0
!Feed(3) = 0.031536*1000.0
!Feed(4) = 0.002995*1000.0

pvap(1) = (10.0**(8.790932 - 1825.357/(Temp-157.209)))*0.007500617    !mmHg
pvap(2) = (10.0**(8.790932 - 1825.357/(Temp-157.209)))*0.007500617    !mmHg
pvap(3) = (exp(18.5875 - 3626.55/((Temp-34.29))))
pvap(4) = (exp(17.2392 - 4487.04/(Temp-140.2)))


do i = 1,4
   fvec(i) = x(i)*pvap(i) - x(i+4)*Ptot
end do

do i = 1,4
   fvec(i+4) = x(i)*x(9) + x(i+4)*x(10) - Feed(i)
end do

fvec(9) = x(1) + x(2) + x(3) + x(4) - 1.0
fvec(10) = x(5) + x(6) + x(7) + x(8) - 1.0

end subroutine
```

The Antoine constant were used to find the vapour pressure of the respective substance at the specified temperature. These in turn were used with Equation 1, Equation 2 and the molar feed values to determine the composition of the vapour and the liquid at the specified temperature. The following tables represent the output data from the program for all three scenarios.

Table B-4 Data obtained for Scenario 1

Molar Ratio	3:1					
Feed Data		**Program Data**			**50 %**	
	mol/hr		**mol/hr**	**92**	**110**	**140**
Biodiesel	7.80126	**Liquid**	**Biodiesel**	7.80000	7.79990	7.79841
SFO	2.60042		**SFO**	2.60000	2.59997	2.59947
Meth	7.80126		**Meth**	7.64749	3.46349	1.32126
Glyc	2.60042		**Glyc**	2.60000	2.59974	2.59656
		Total Liquid		20.64748	16.46309	14.31570
		Vapour	**Biodiesel**	0.00000	0.00010	0.00159
			SFO	0.00000	0.00003	0.00053
			Meth	0.15251	4.33651	6.47874
			Glyc	0.00000	0.00026	0.00344
		Total Vapour		0.15252	4.33691	6.48430
Feed Data		**Program Data**			**60%**	
	mol/hr		**mol/hr**	**92**	**110**	**140**
Biodiesel	9.36151	**Liquid**	**Biodiesel**	9.36001	9.35994	9.35875
SFO	2.08034		**SFO**	2.08000	2.07999	2.07972
Meth	6.24101		**Meth**	8.56520	3.87915	1.47996
Glyc	3.12050		**Glyc**	3.12003	3.11985	3.11729
		Total Liquid		23.12524	18.43893	16.03572
		Vapour	**Biodiesel**	-0.00001	0.00006	0.00125
			SFO	0.00000	0.00001	0.00028
			Meth	-2.32520	2.36084	4.76004
			Glyc	-0.00003	0.00015	0.00271
		Total Vapour		-2.32524	2.36107	4.76428

Table B-5 Data obtained for Scenario 2

Molar Ratio	4:1					
Feed Data		**Program Data**			**50%**	
	mol/hr		**mol/hr**	**92**	**110**	**140**
Biodiesel	7.80126	**Liquid**	**Biodiesel**	7.79998	7.79977	7.79713
SFO	2.60042		**SFO**	2.59999	2.59992	2.59904
Meth	13.00210		**Meth**	7.64744	3.46337	1.32081
Glyc	2.60042		**Glyc**	2.59994	2.59942	2.59379
		Total Liquid		20.64735	16.46248	14.31078
		Vapour	**Biodiesel**	0.00002	0.00023	0.00287
			SFO	0.00001	0.00008	0.00096
			Meth	5.35256	9.53663	11.67919
			Glyc	0.00006	0.00058	0.00621
		Total Vapour		5.35265	9.53752	11.68922
Feed Data		**Program Data**			**60%**	
	mol/hr		**mol/hr**	**92**	**110**	**140**
Biodiesel	9.36151	**Liquid**	**Biodiesel**	9.35999	9.35980	9.35738
SFO	2.08034		**SFO**	2.08000	2.07996	2.07942
Meth	11.44185		**Meth**	8.56515	3.87902	1.47949
Glyc	3.12050		**Glyc**	3.11997	3.11951	3.11433
		Total Liquid		23.12510	18.43829	16.03062
		Vapour	**Biodiesel**	0.00001	0.00020	0.00262
			SFO	0.00000	0.00004	0.00058
			Meth	2.87485	7.56098	9.96051
			Glyc	0.00003	0.00049	0.00567
		Total Vapour		2.87490	7.56171	9.96938

Table B-6 Data obtained for Scenario 3

Molar Ratio	20:1					
Feed Data		**Program Data**			**50%**	
	mol/hr		**mol/hr**	**90**	**110**	**140**
Biodiesel	14.82240	**Liquid**	**Biodiesel**	14.81988	14.81882	14.80698
SFO	0.26004		**SFO**	0.26000	0.25998	0.25977
Meth	44.98727		**Meth**	13.12075	5.33275	2.03118
Glyc	4.94080		**Glyc**	4.93965	4.93703	4.91189
		Total Liquid		33.14028	25.34858	22.00982
		Vapour	**Biodiesel**	0.00012	0.00118	0.01302
			SFO	0.00000	0.00002	0.00023
			Meth	31.86925	39.65725	42.95882
			Glyc	0.00035	0.00297	0.02811
		Total Vapour		31.86972	39.66142	43.00018
Feed Data		**Program Data**			**60%**	
	mol/hr		**mol/hr**	**90**	**110**	**140**
Biodiesel	14.97842	**Liquid**	**Biodiesel**	14.97991	14.97909	14.96969
SFO	0.20803		**SFO**	0.21000	0.20999	0.20986
Meth	35.98982		**Meth**	13.22570	5.37563	2.04832
Glyc	4.99281		**Glyc**	4.98975	4.98770	4.96773
		Total Liquid		33.40536	25.55241	22.19559
		Vapour	**Biodiesel**	0.00009	0.00091	0.01031
			SFO	0.00000	0.00001	0.00014
			Meth	22.76430	30.61437	33.94168
			Glyc	0.00025	0.00230	0.02227
		Total Vapour		22.76464	30.61759	33.97441

C Appendix C – Commissioning Run Data

C.1 Data from Commissioning Runs

The set flowrate for the Commissioning Runs was 4l/hr. The various results for the pre-reactor (Pre.) and reboiler (Reb.) are displayed. The viscosity times were used to calculate the respective viscosities using Equation 6 and Equation 7.

Run 1: Temperature – 70^{o}C, Ratio – 3:1

Run 1	Viscosity Time(s)		Viscosity (mm2/s)		% Conversion		Level	Res Time
Time	Pre.	Reb.	Pre.	Reb.	Pre.	Reb.	(mm)	(mins)
0	419.8	494.7	43.4	51.2	16.7	9.6	290	41.4
20	517.8	524.8	53.6	54.3	7.6	7.0	320	45.5
40	533.2	497.8	55.2	51.5	6.3	9.3	300	42.8
60	537.8	500.3	55.7	51.8	6.0	9.1	365	51.7
80	480.0	511.9	49.7	53.0	10.9	8.1	340	48.3
100	398.3	514.3	41.2	53.2	19.0	7.9	300	42.8
120	393.3	460.7	40.7	47.7	19.6	12.7	235	33.8
140	457.5	489.3	47.3	50.6	13.0	10.1	190	27.6
160	368.5	434.6	38.1	45.0	22.4	15.2	115	17.2
180	336.3	404.2	34.8	41.8	26.4	18.4	65	10.3

Run 2: Temperature – 70^{o}C, Ratio – 3:1

Run 2	Viscosity Time(s)		Viscosity (mm2/s)		% Conversion		Level	Res Time
Time	Pre.	Reb.	Pre.	Reb.	Pre.	Reb.	(mm)	(mins)
0	326.1	216.6	33.7	22.4	27.7	45.5	50	8.3
20	269.6	229.8	27.9	23.8	36.0	42.9	110	16.6
40	268.7	268.3	27.8	27.8	36.1	36.2	65	10.3
60	246.5	230.3	25.5	23.8	39.9	42.9	100	15.2
80	307.2	194.1	31.8	20.1	30.3	50.3	55	9.0
100	234.1	208.3	24.2	21.6	42.1	47.2	80	12.4
120	265.3	210.8	27.4	21.8	36.7	46.7	55	9.0
140	345.2	230.5	35.7	23.9	25.2	42.8	180	26.2
160	252.5	217.6	26.1	22.5	38.8	45.3	80	12.4
180	248.1	184.2	25.7	19.1	39.6	52.6	20	4.1

Run 3: Temperature – 70^{o}C, Ratio – 3:1

Run 3	Viscosity Time(s)		Viscosity (mm2/s)		% Conversion		Level	Res Time
Time	Pre.	Reb.	Pre.	Reb.	Pre.	Reb.	(mm)	(mins)
0	288.5	200.1	29.9	20.7	33.0	49.0	30	5.5
20	228.1	190.4	23.6	19.7	43.3	51.1	55	9.0
40	227.9	163.0	23.6	16.9	43.3	57.9	80	12.4
60	212.3	154.2	22.0	16.0	46.4	60.3	95	14.5
80	210.9	153.3	21.8	15.9	46.7	60.5	110	16.6
100	190.3	150.4	19.7	15.6	51.2	61.4	120	17.9
120	180.7	137.9	18.7	14.3	53.4	65.2	80	12.4
140	131.0	139.6	13.6	14.4	67.4	64.6	30	5.5
160	123.9	118.2	12.8	12.2	69.8	71.9	50	8.3
180	193.9	116.8	20.1	12.1	50.3	72.4	30	5.5

Run 4: Temperature – 70^{o}C, Ratio – 3:1

Run 4	Viscosity Time(s)		Viscosity (mm2/s)		% Conversion		Level	Res Time
Time	Pre.	Reb.	Pre.	Reb.	Pre.	Reb.	(mm)	(mins)
0	238.4	183.7	24.7	19.0	41.3	52.7	120	17.9
20	292.3	180.1	30.2	18.6	32.5	53.5	300	42.8
40	263.5	213.4	27.3	22.1	37.0	46.2	310	44.1
60	232.7	223.1	24.1	23.1	42.4	44.2	280	40.0
80	280.6	212.6	29.0	22.0	34.3	46.3	330	46.9
100	323.5	225.2	33.5	23.3	28.1	43.8	120	17.9
120	282.1	225.8	29.2	23.4	34.0	43.7	330	46.9
140	255.3	223.6	26.4	23.1	38.4	44.1	130	19.3
160	261.4	220.8	27.1	22.8	37.3	44.7	300	42.8
180	257.8	224.0	26.7	23.2	37.9	44.1	210	30.3

Run 5: Temperature – 70^{o}C, Ratio – 3:1

Run 5	Viscosity Time(s)		Viscosity (mm2/s)		% Conversion		Level	Res Time
Time	Pre.	Reb.	Pre.	Reb.	Pre.	Reb.	(mm)	(mins)
0	179.4	164.1	18.6	17.0	53.7	57.6	90	13.8
20	158.9	176.7	16.4	18.3	59.0	54.4	100	15.2
40	178.1	146.5	18.4	15.2	54.0	62.5	100	15.2
60	184.8	137.2	19.1	14.2	52.4	65.4	115	17.2
80	192.5	134.7	19.9	13.9	50.6	66.2	155	22.8
100	171.6	129.9	17.8	13.4	55.6	67.8	200	29.0
120	175.1	135.5	18.1	14.0	54.8	65.9	205	29.7
140	187.0	131.4	19.3	13.6	51.9	67.2	210	30.3
160	140.4	130.9	14.5	13.6	64.4	67.4	217	31.3
180	193.4	133.2	20.0	13.8	50.5	66.7	225	32.4

Run 6: Temperature – 70^{o}C →90 ^{o}C, Ratio – 3:1

Run 6	Viscosity Time(s)		Viscosity (mm2/s)		% Conversion		Level	Res Time
Time	Pre.	Reb.	Pre.	Reb.	Pre.	Reb.	(mm)	(mins)
0	288.8	218.1	29.9	22.6	33.0	45.2	260	37.2
20	285.1	230.8	29.5	23.9	33.6	42.8	100	15.2
40	286.2	239.5	29.6	24.8	33.4	41.2	100	15.2
60	299.6	258.7	31.0	26.8	31.4	37.8	115	17.2
80	289.3	270.0	29.9	27.9	32.9	35.9	155	22.8
100	296.8	263.7	30.7	27.3	31.8	37.0	200	29.0
120	284.7	272.8	29.5	28.2	33.6	35.5	205	29.7
140	316.5	277.1	32.8	28.7	29.0	34.8	210	30.3
160	309.1	273.0	32.0	28.2	30.1	35.5	217	31.3
180	271.4	275.3	28.1	28.5	35.7	35.1	225	32.4

C.2 **Mass Balance Calculations**

The below Table C-1 is the spreadsheet used to enter the data taken during the run and calculate the mass balance for the specific run.

Table C-1 Representation of Mass Balance Data

				Density	Oil	912.7	g/l
					Biodiesel	868.0	g/l
					Meth & KOH	780.8	g/l
Run		**P2**		**P3**		**P4**	
IN							
		(l)	***(g)***	***(l)***	***(g)***	***(l)***	***(g)***
Oil	Feed	11.5	10495.67	9	8214	9.443	8618.311
	Primer	1.95	1779.7	1.5	1369	1.5	1369
Meth	Feed	1.48	1155.568	1.195	933.0434	1.278	998
	Primer	0.26	203.0053	0.19	148.35	0.19	148
Biodiesel	Primer	3	2604	2.5	2170	2.5	2170
Total			**16238**		**12834**		**13304**
OUT	Product		**16195**		**12772**		**13284**
Difference			**-43**		**-62**		**-20**

D Appendix D – Result Calculations

D.1 Residence Time Calculations

A spreadsheet was used to calculate the respective pre-reactor residence times for the respective runs. The below table illustrates the calculations.

Table D-1 Calculated pre-reactor residence times for all runs

Residence Time Calculator			Run	Flow Rate (l/hr)	Level (mm)	Res Time (min)
Constants			T1	4.0	199	29
Column D	108.2	mm	T2	3.9	244	36
Column R	54.1	mm	T3	4.7	240	29
			T4	4.5	220	28
Add. Height from flange			T5	4.5	220	28
	10	mm	T6	3.8	242	37
			T7	3.2	223	40
Conv. Factor			T8	3.2	223	40
mm3-ltr			T9	4.5	190	24
0.000001			T10	5.3	100	12
hr-min			P1	4.5	169	22
60			P2	4.3	166	22
			P3	3.4	220	37
			P4	3.6	206	33

D.2 **Molar Ratio and Flowrate Calculations**

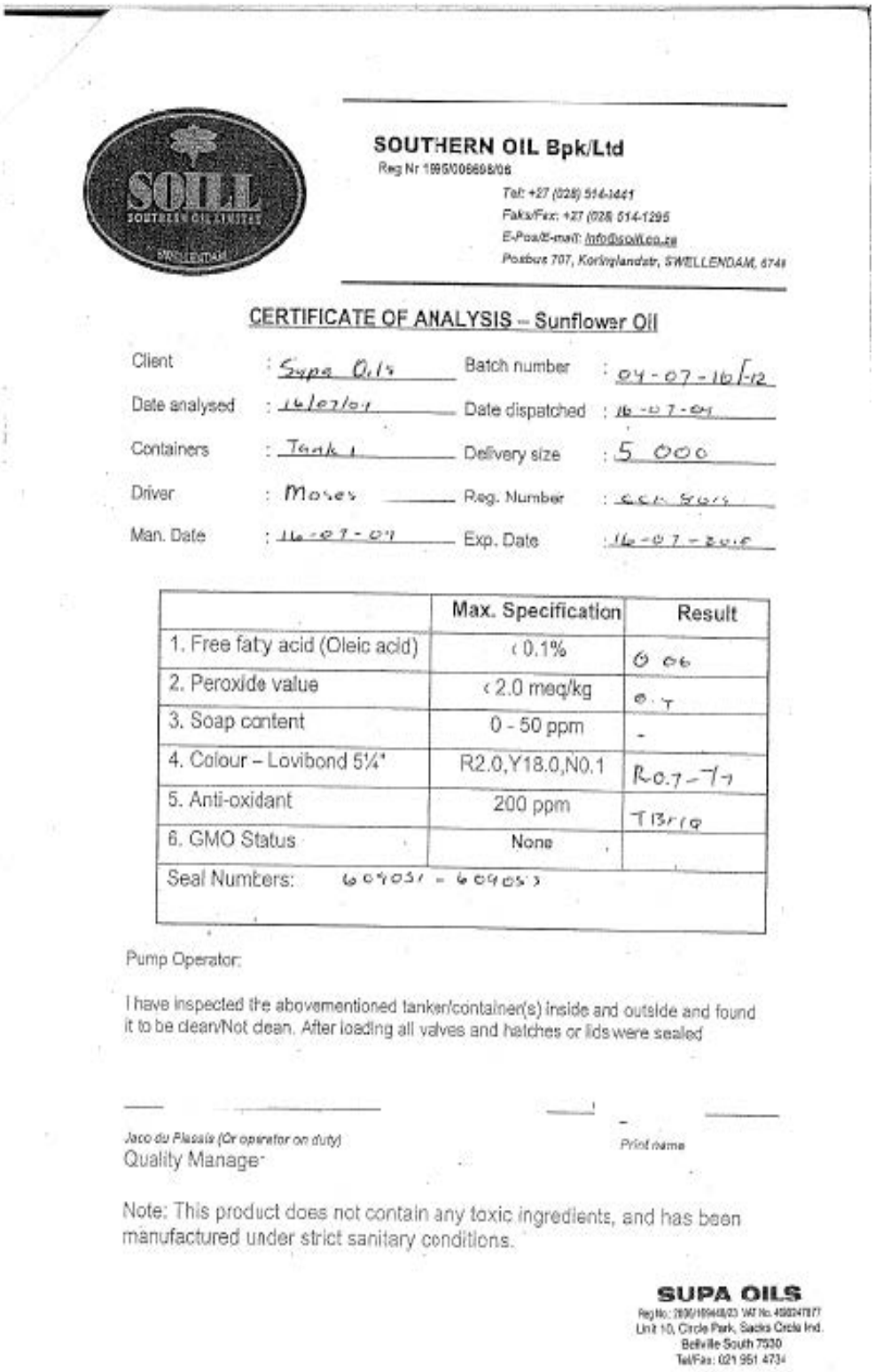
The following spreadsheet reports the data captured and use to calculate the molar ratios and flowrates for the respective runs

Table D-2 Flowrate and Molar Ratio Calculation

Run	Oil Used (l)	Methanol Used (l)	Ratio – Meth: Oil	Run Time (hr)	Flowrate Total (l/hr)
T1	10.0	1.92	4.5	3	4.0
T2	10.0	1.60	3.9	3	3.9
T3	12.0	2.05	4.0	3	4.7
T4	12.0	1.54	3.0	3	4.5
T5	12.0	1.57	3.1	3	4.5
T6	10.0	1.32	3.1	3	3.8
T7	8.5	1.08	3.1	3	3.2
T8	8.5	1.12	3.0	3	3.2
T9	12.0	1.52	3.0	3	4.5
T10	14.0	1.79	3.1	3	5.3
P1	12.0	1.52	3.0	3	4.5
P2	11.5	1.48	3.0	3	4.3
P3	9.0	1.20	3.1	3	3.4
P4	9.4	1.28	3.2	3	3.6

E Appendix E – Sunflower Oil Specification Sheet

Specification sheet for the sunflower oil used in this project



SOUTHERN OIL Bpk/Ltd
Reg Nr 1995/009698/06
Tel: +27 (028) 514-1441
Faks/Fax: +27 (028) 514-1295
E-Pos/E-mail: info@soil.co.za
Posbus 707, Korinplandstr, SWELLENDAM, 6740

CERTIFICATE OF ANALYSIS – Sunflower Oil

Client	: Supa Oils	Batch number	: 04-07-16/-12
Date analysed	: 16/07/07	Date dispatched	: 16-07-07
Containers	: Tank 1	Delivery size	: 5 000
Driver	: Moses	Reg. Number	: CCL 5021
Man. Date	: 16-07-07	Exp. Date	: 16-07-2008

	Max. Specification	Result
1. Free fatty acid (Oleic acid)	< 0.1%	0.06
2. Peroxide value	< 2.0 meq/kg	0.7
3. Soap content	0 - 50 ppm	-
4. Colour – Lovibond 5¼"	R2.0,Y18.0,N0.1	R0.7-7.1
5. Anti-oxidant	200 ppm	TBHQ
6. GMO Status	None	
Seal Numbers:	609051 - 609053	

Pump Operator:

I have inspected the abovementioned tanker/container(s) inside and outside and found it to be clean/Not clean. After loading all valves and hatches or lids were sealed

Jaco du Plessis (Or operator on duty)
Quality Manager

Print name

Note: This product does not contain any toxic ingredients, and has been manufactured under strict sanitary conditions.

SUPA OILS
Reg No.: 2000/18948/23 VAT No. 4080247877
Unit 10, Circle Park, Sacks Circle Ind.
Bellville South 7530
Tel/Fax: 021 951 4734

F Appendix F – Experimental Run Data

All data captured from runs

Run	T1																			
Time	Level		P.R Res. T	Temp	Time (s)		Viscocity (mm2/s)								% Conversion					
(mins)	(mm)	Avg	(mins)		Preactor	Reboiler	Prereactor	Avg	Reboiler	Avg	Delta conv %	Avg	Difference	Avg	Pre Reactor	Reboiler				
0	220	199.17	29	90.00	115.69	107.90	11.97	11.39	11.17	9.59					72.78	75.81				
20	200			90.00	108.31	102.93	11.21		10.65		6.53	9.04	5.08	7.51	75.65	77.86				
40	165			90.00	107.81	96.50	11.16		9.99		6.22		5.02		75.85	80.67				
60	193			89.00	114.41	93.34	11.84		9.66		7.63		6.27		73.27	82.11				
80	205			91.00	106.75	90.19	11.05		9.33		12.37		10.34		76.28	83.61				
100	212			91.00	107.28	86.69	11.10		8.97		10.61		9.05		76.06	85.33				
120	216			91.00	117.35	86.67	12.14		8.97		10.87		9.28		72.16	85.34				
140	200			91.00	129.96	89.75	13.45		9.29		13.91		11.66		67.72	83.82				
160	125			91.00	113.69	92.90	11.77		9.61		17.73		14.60		73.54	82.32				
180	125			91.00	116.24	91.59	12.03		9.48		11.33		9.40		72.58	82.94				
Run	T2																			
Time	Level		P.R Res. T	Temp	Time (s)		Viscocity (mm2/s)								% Conversion					
(mins)	(mm)	Avg	(mins)		Preactor	Reboiler	Prereactor	Avg	Reboiler	Avg	Delta conv %	Avg	Difference	Avg	Pre Reactor	Reboiler				
0	140	243.75	36	91.00	170.25	132.50	17.62	18.62	13.71	13.77					55.98	66.88				
20	190			91.00	141.06	152.00	14.60		15.73		8.09	19.61	4.93	13.24	64.16	60.91				
40	250			92.00	181.12	146.68	18.74		15.18		-2.72		-1.70		53.29	62.46				
60	255			91.00	175.03	146.16	18.11		15.13		14.89		9.32		54.78	62.62				
80	230			91.00	179.22	135.97	18.55		14.07		16.70		10.98		53.75	65.76				
100	240			91.00	184.46	130.03	19.09		13.46		20.61		13.95		52.50	67.70				
120	250			91.00	173.12	120.00	17.92		12.42		26.26		18.69		55.26	71.19				
140	260			91.00	199.28	152.03	20.62		15.73		9.27		5.65		49.14	60.90				
160	270			91.00	184.19	154.00	19.06		15.94		18.57		11.21		52.56	60.34				
180	220			91.00	139.64	133.07	14.45		13.77		21.19		14.13		64.60	66.70				
Run	T3																			
Time	Level		P.R Res. T	Temp	Time (s)		Viscocity (mm2/s)								% Conversion					
(mins)	(mm)	Avg	(mins)		Preactor	Reboiler	Prereactor	Avg	Reboiler	Avg	Delta conv %	Avg	Difference	Avg	Pre Reactor	Reboiler				
20	250	240.00	29	92.00	169.03	107.56	17.49	18.54	11.13	16.14					56.30	75.95				
40	260			91.00	168.97	127.13	17.49		13.16		18.03	9.90	12.39	5.99	56.31	68.68				
60	230			91.00	167.28	142.41	17.31		14.74		11.66		7.44		56.75	63.75				
80	220			91.00	185.37	163.00	19.18		16.87		1.95		1.13		52.28	57.88				
100	260			91.00	171.65	160.38	17.76		16.60		10.75		6.30		55.63	58.58				
120	250			91.00	192.16	149.41	19.89		15.46		9.78		6.03		50.72	61.66				
140	220			91.00	169.47	150.97	17.54		15.62		17.14		10.49		56.18	61.21				
160	230			92.00	175.18	163.07	18.13		16.88		2.89		1.67		54.74	57.86				
180	260			91.00	170.00	151.31	17.59		15.66		10.42		6.37		56.05	61.11				

Run	T4															
Time	Level		P.R Res. Ti	Temp	Time (s)		Viscocity (mm2/s)								% Conversion	
(mins)	(mm)	Avg	(mins)		Preactor	Reboiler	Prereactor	Avg	Reboiler	Avg	Delta conv %	Avg	Difference	Avg	Pre Reactor	Reboiler
20	140	220.00	28	91.00	186.78	136.41	19.33	**18.05**	14.12	**16.20**					51.95	65.62
40	180			111.00	177.53	157.12	18.37		16.26		12.64	**7.82**	7.52	**4.69**	54.16	59.47
60	220			110.00	161.22	161.28	16.68		16.69		7.15		4.17		58.35	58.34
80	260	157.12	178	110.00	176.10	159.62	18.22		16.52		0.74		0.43		54.51	58.79
100	300			112.00	170.66	158.03	17.66		16.35		7.95		4.71		55.88	59.22
120	270			111.00	159.66	146.50	16.52		15.16		10.62		6.64		58.78	62.52
140	280			111.00	158.13	157.94	16.36		16.34		0.79		0.47		59.19	59.25
160	260			111.00	189.75	145.94	19.64		15.10		5.56		3.49		51.27	62.68
180	250			111.00	163.19	154.09	16.89		15.95		15.00		9.05		57.82	60.32

Run	T5															
Time	Level		P.R Res. Ti	Temp	Time (s)		Viscocity (mm2/s)								% Conversion	
(mins)	(mm)	Avg	(mins)		Preactor	Reboiler	Prereactor	Avg	Reboiler	Avg	Delta conv %	Avg	Difference	Avg	Pre Reactor	Reboiler
20	140	220.00	28	140.00	157.38	134.81	16.29	**18.69**	13.95	**16.29**					59.40	66.13
40	140			140.00	179.09	153.10	18.53		15.84		1.98	**9.98**	1.20	**5.91**	53.78	60.60
60	180			141.00	190.44	157.32	19.71		16.28		9.48		5.64		51.11	59.42
80	220			141.00	177.02	158.62	18.32		16.41		13.46		7.95		54.29	59.06
100	250			141.00	181.06	158.19	18.74		16.37		8.26		4.89		53.31	59.18
120	300			140.00	192.72	158.91	19.94		16.44		9.62		5.67		50.59	58.98
140	230			141.00	163.09	159.91	16.88		16.55		13.82		8.11		57.85	58.71
160	260			141.00	146.72	151.53	15.18		15.68		5.24		3.20		62.45	61.05
180	280			141.00	154.63	164.57	16.00		17.03		-8.69		-4.99		60.17	57.46

Run	T6															
Time	Level		P.R Res. Ti	Temp	Time (s)		Viscocity (mm2/s)								% Conversion	
(mins)	(mm)	Avg	(mins)		Preactor	Reboiler	Prereactor	Avg	Reboiler	Avg	Delta conv %	Avg	Difference	Avg	Pre Reactor	Reboiler
20	220	241.67	37	111.00	141.69	138.34	14.66	**18.27**	14.32	**14.92**					63.97	65.01
40	190			110.00	132.38	149.44	13.70		15.46		-3.76	**13.72**	-2.32	**8.67**	66.92	61.65
60	210			111.00	161.75	152.40	16.74		15.77		-10.07		-6.12		58.21	60.80
80	240			111.00	188.56	150.12	19.51		15.53		5.28		3.24		51.54	61.45
100	280			110.00	156.06	142.93	16.15		14.79		18.94		12.05		59.77	63.59
120	250			110.00	181.57	138.50	18.79		14.33		7.99		5.19		53.18	64.96
140	270			110.00	170.59	139.50	17.65		14.44		17.73		11.46		55.90	64.64
160	200			110.00	201.00	142.12	20.80		14.71		12.44		7.94		48.76	63.84
180	200			110.00	224.53	151.94	23.24		15.72		19.97		12.17		43.95	60.93

Run	T7															
Time	Level		P.R Res. Ti	Temp	Time (s)		Viscocity (mm2/s)								% Conversion	
(mins)	(mm)	Avg	(mins)		Preactor	Reboiler	Prereactor	Avg	Reboiler	Avg	Delta conv %	Avg	Difference	Avg	Pre Reactor	Reboiler
20	160	222.86	40	71.00	184.47	132.00	19.09	**17.01**	13.66	**15.73**					52.50	67.05
40	150			71.00	156.81	145.34	16.23		15.04		16.49	**5.49**	10.37	**3.38**	59.56	62.86
60	220			71.00	168.75	158.62	17.46		16.41		-0.84		-0.50		56.37	59.06
80	300			71.00	158.94	156.69	16.45		16.21		5.41		3.22		58.97	59.59
100	170			71.00	162.44	152.25	16.81		15.76		3.07		1.87		58.03	60.84
120	270			71.00	183.21	147.78	18.96		15.29		6.62		4.11		52.79	62.14
140	220			71.00	163.91	149.31	16.96		15.45		14.42		8.90		57.63	61.69
160	230			71.00	156.78	148.53	16.22		15.37		6.92		4.28		59.57	61.92
180	220			71.00	183.10	150.62	18.95		15.59		2.84		1.74		52.82	61.31
Run	T8															
Time	Level		P.R Res. Ti	Temp	Time (s)		Viscocity (mm2/s)								% Conversion	
(mins)	(mm)	Avg	(mins)		Preactor	Reboiler	Prereactor	Avg	Reboiler	Avg	Delta conv %	Avg	Difference	Avg	Pre Reactor	Reboiler
20	180	222.50	40	71.00	157.75	133.82	16.32	**15.88**	13.85	**14.75**					59.30	66.45
40	210			71.00	152.60	140.94	15.79		14.58		7.63	**4.84**	4.90	**3.11**	60.74	64.20
60	250			70.00	144.59	148.09	14.96		15.32		2.10		1.30		63.09	62.05
80	210			71.00	150.91	145.69	15.62		15.08		-0.53		-0.33		61.23	62.76
100	250			71.00	139.21	140.60	14.41		14.55		4.78		3.08		64.73	64.30
120	260			71.00	177.03	140.35	18.32		14.52		-0.55		-0.35		54.29	64.38
140	170			71.00	163.19	142.88	16.89		14.79		14.65		9.32		57.82	63.60
160	250			71.00	142.53	137.00	14.75		14.18		11.62		7.61		63.71	65.43
180	200			71.00	154.27	144.57	15.96		14.96		-0.98		-0.62		60.27	63.09
Run	T9															
Time	Level		P.R Res. Ti	Temp	Time (s)		Viscocity (mm2/s)								% Conversion	
(mins)	(mm)	Avg	(mins)		Preactor	Reboiler	Prereactor	Avg	Reboiler	Avg	Delta conv %	Avg	Difference	Avg	Pre Reactor	Reboiler
20	100	190.00	24	130.00	273.71	205.50	28.32	**20.65**	21.27	**16.64**					35.34	47.80
40	120			117.00	211.59	183.75	21.90		19.02		32.90	**15.96**	17.33	**9.39**	46.53	52.67
60	140			110.00	191.66	165.69	19.83		17.15		18.60		10.63		50.83	57.16
80	160			93.00	200.59	169.62	20.76		17.55		9.46		5.31		48.85	56.14
100	200			96.00	195.72	167.81	20.25		17.37		13.70		7.76		49.92	56.61
120	240			92.00	210.65	162.37	21.80		16.80		13.99		8.12		46.73	58.04
140	220			93.00	200.10	151.12	20.71		15.64		23.61		14.44		48.96	61.17
160	250			91.00	186.50	157.97	19.30		16.35		17.35		10.28		52.02	59.24
180	230			91.00	185.28	151.06	19.17		15.63		14.98		9.16		52.31	61.18

Run	T10															
Time	Level		P.R Res. Ti	Temp	Time (s)		Viscocity (mm2/s)								% Conversion	
(mins)	(mm)	Avg	(mins)		Preactor	Reboiler	Prereactor	Avg	Reboiler	Avg	Delta conv %	Avg	Difference	Avg	Pre Reactor	Reboiler
0	110	100.00	12	25.00	181.41	140.06	18.77	18.43	14.49	15.29					53.22	64.47
10	100			25.00	151.38	149.31	15.67		15.45		13.72	12.81	8.47	7.86	61.09	61.69
20	90			25.00	201.59	139.09	20.86		14.39		5.68		3.68		48.64	64.77
30	90			24.00	159.25	155.00	16.48		16.04		19.02		11.43		58.89	60.06
40	90	102.50	12	34.00	178.60	163.60	18.48	17.91	16.93	15.73					53.90	57.72
50	100			41.00	196.13	154.12	20.30		15.95		10.63	9.00	6.41	5.48	49.83	60.31
60	100			35.00	157.85	153.47	16.33		15.88		17.63		10.66		59.27	60.49
70	120			34.00	159.53	155.28	16.51		16.07		1.19		0.71		58.81	59.99
80	140			32.00	138.25	145.10	14.31		15.02		6.55		4.12		65.04	62.93
90	170	190.00	21	40.00	140.10	147.09	14.50	14.92	15.22	14.21					64.46	62.34
100	180			54.00	141.47	143.72	14.64		14.87		-1.75	3.19	-1.11	2.12	64.03	63.35
110	200			49.00	146.81	134.85	15.19		13.95		3.15		2.08		62.42	66.12
120	210			41.00	148.19	136.56	15.34		14.13		4.80		3.15		62.02	65.57
130	220			41.00	130.72	134.03	13.53		13.87		6.58		4.37		67.47	66.38
140	230	210.00	23	52.00	152.16	135.31	15.75	15.54	14.00	13.00					60.87	65.97
150	240			58.00	147.81	130.30	15.30		13.48		9.97	11.21	6.74	7.77	62.13	67.61
160	170			49.00	143.75	117.94	14.88		12.20		13.64		9.82		63.34	71.94
170	200			58.00	157.03	123.34	16.25		12.76		9.51		6.66		59.50	70.00
180	210			52.00	140.56	131.00	14.55		13.56		11.70		7.88		64.32	67.38
Run	P1															
Time	Level		P.R Res. Ti	Temp	Time (s)		Viscocity (mm2/s)								% Conversion	
(mins)	(mm)	Avg	(mins)		Preactor	Reboiler	Prereactor	Avg	Reboiler	Avg	Delta conv %	Avg	Difference	Avg	Pre Reactor	Reboiler
20	200	168.57	22	91.00	166.34	130.88	17.21	**17.59**	13.54	**14.82**					56.99	67.42
40	110			92.00	179.12	152.50	18.54		15.78		6.22	**11.52**	3.78	**7.36**	53.78	60.77
60	90			91.00	157.66	130.12	16.32		13.47		20.53		13.90		59.32	67.67
80	110			90.00	189.41	152.22	19.60		15.75		2.51		1.53		51.35	60.85
100	140			90.00	178.09	145.56	18.43		15.06		18.23		11.45		54.03	62.80
120	200			91.00	158.37	145.72	16.39		15.08		13.90		8.72		59.13	62.75
140	210			91.00	175.50	142.69	18.16		14.77		7.12		4.53		54.66	63.66
160	230			91.00	176.03	142.62	18.22		14.76		14.16		9.02		54.53	63.68
180	200			91.00	154.50	134.66	15.99		13.94		17.60		11.65		60.20	66.18

Run	P2															
Time	Level		P.R Res. Ti	Temp	Time (s)		Viscocity (mm2/s)								% Conversion	
(mins)	(mm)	Avg	(mins)		Preactor	Reboiler	Prereactor	Avg	Reboiler	Avg	Delta conv %	Avg	Difference	Avg	Pre Reactor	Reboiler
20	140	166.25	22	92.00	190.70	138.31	19.73	**18.57**	14.31	**15.57**					51.05	65.02
40	110			91.00	184.47	158.81	19.09		16.43		13.48	**12.46**	7.96	**7.63**	52.50	59.01
60	110			91.00	195.50	150.84	20.23		15.61		14.29		8.75		49.97	61.25
80	140			91.00	182.50	157.16	18.89		16.26		15.96		9.49		52.96	59.46
100	170			91.00	171.28	151.16	17.72		15.64		13.40		8.19		55.72	61.15
120	200			91.00	167.66	150.16	17.35		15.54		9.31		5.72		56.65	61.44
140	230			91.00	170.28	149.13	17.62		15.43		8.25		5.09		55.98	61.74
160	230			91.00	173.56	140.16	17.96		14.50		13.13		8.46		55.15	64.44
180	210			91.00	152.69	146.40	15.80		15.15		11.83		7.40		60.72	62.55

Run	P3															
Time	Level		P.R Res. Ti	Temp	Time (s)		Viscocity (mm2/s)								% Conversion	
(mins)	(mm)	Avg	(mins)		Preactor	Reboiler	Prereactor	Avg	Reboiler	Avg	Delta conv %	Avg	Difference	Avg	Pre Reactor	Reboiler
20.00	190.00	220.00	37.34	110.00	158.66	112.97	16.42	**15.99**	11.69	**14.10**					59.05	73.82
40.00	230.00			110.00	148.68	133.63	15.39		13.83		11.22	**8.18**	7.46	**5.37**	61.87	66.51
60.00	210.00			111.00	135.15	136.52	13.99		14.13		5.66		3.71		66.02	65.58
80.00	230.00			111.00	164.37	131.47	17.01		13.60		1.79		1.20		57.51	67.22
100.00	230.00			111.00	169.65	137.81	17.56		14.26		11.76		7.66		56.14	65.17
120.00	230.00			111.00	149.18	137.03	15.44		14.18		14.19		9.28		61.73	65.42
140.00	200.00			111.00	157.65	140.65	16.31		14.55		3.98		2.56		59.33	64.29
160.00	240.00			111.00	152.44	138.44	15.78		14.33		8.69		5.65		60.79	64.98
180.00	230.00			111.00	152.06	134.59	15.74		13.93		8.18		5.41		60.90	66.20

Run	P4															
Time	Level		P.R Res. Ti	Temp	Time (s)		Viscocity (mm2/s)								% Conversion	
(mins)	(mm)	Avg	(mins)		Preactor	Reboiler	Prereactor	Avg	Reboiler	Avg	Delta conv %	Avg	Difference	Avg	Pre Reactor	Reboiler
20.00	140.00	206.25	33.38	71.00	124.47	118.44	12.88	**14.04**	12.26	**13.74**					69.60	71.76
40.00	160.00			71.00	157.97	127.53	16.35		13.20		-1.54	**1.14**	-1.06	**0.77**	59.24	68.54
60.00	210.00			71.00	127.22	133.75	13.17		13.84		10.89		7.24		68.65	66.47
80.00	240.00			71.00	143.81	138.00	14.88		14.28		-5.43		-3.54		63.32	65.11
100.00	230.00			71.00	126.15	135.03	13.05		13.97		4.15		2.74		69.02	66.06
120.00	210.00			71.00	132.44	132.10	13.71		13.67		-2.99		-2.00		66.90	67.01
140.00	230.00			71.00	122.94	131.78	12.72		13.64		0.32		0.22		70.14	67.12
160.00	230.00			71.00	150.06	133.00	15.53		13.76		-5.13		-3.42		61.47	66.72
180.00	220.00			71.00	124.19	130.84	12.85		13.54		8.84		5.96		69.70	67.43